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TOXICITY TREATABILITY
OF
IRON AND STEEL PLANT WASTEWATERS
A RESOURCE DOCUMENT

by

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16. ABSTRACT

The report gives results of an assessment of the toxicity treatability of wastewaters from eight steelmaking subcategories, all considered assessable under the somewhat low production levels of the study period. Tests were conducted using prescribed procedures for conventional water contaminants, toxic organics, and static bioassay. Samples were collected before and after units of the wastewater treatment systems. All tests were done under the auspices of a quality assurance program. Efforts were made to ensure representativeness of all samples; e.g., if the production facilities were operating only one turn, samples were collected only during that turn. Results show the relative toxicity and variability of wastewaters from the different manufacturing subcategories and the reductions in toxicity. Relationships between pollutant content and toxicity are examined with cognizance of the possible site uniqueness of the data.

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ABSTRACT

As part of its toxic pollutant control program, the Environmental Protection Agency (EPA) has gathered information about priority toxic pollutants in wastewaters discharged by the iron and steel industry (46 FR 1858). Little information is available, however, on the effects of these pollutants and their combinations on bioassay (toxicity) test species. Nor is it known how effective the treatment processes identified in model treatment systems may be in reducing their concentrations and the toxic effects.

Because a bioassay can simultaneously assess the effects of numerous toxic pollutants, it is a useful test of overall toxicity and of toxicity reduction resulting from various wastewater treatments. Bioassay data, together with toxic pollutant data and the relevant parameters of the industrial process, can guide the formulation of regulatory strategy and help in the selection of effective treatments that will reduce toxic impacts on receiving waters.

This study assessed the toxicity treatability of wastewaters from eight steelmaking subcategories. The study was limited to those treatment systems considered assessable under the somewhat low production levels of the study period.

Testing programs were conducted using prescribed procedures for conventional water contaminants, toxic organics, and static bioassay. Samples were collected before and after units of the wastewater treatment systems. All testing was done under the auspices of a quality-assurance program. Efforts were made to insure representativeness of all samples. For example, if the production facilities were operating only one turn, samples were collected only during that turn.

The results show the relative toxicity and variability of wastewaters from the different manufacturing subcategories and the reductions in toxicity. Relationships between pollutant content and toxicity are examined with cognizance of the possible site uniqueness of the data.

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LIST OF ABBREVIATIONS FOR WASTEWATER TREATMENTS

A	acidification
AF	air flotation
AO	air oxidation
ASF	free ammonia still
ASFF-L	free and fixed ammonia still-lime addition
BOA-1	one-stage biological reactor
BOA-2	two-stage biological reactor
CAG	carbon adsorption, granular
CL	clarifier
CLA	alkaline chlorination
CNT	central treatment
CPT	chrome pretreatment
CT	cooling tower
CYPT	cyanide pretreatment
DP	dephenolization
DS	desulfurization
E	equalization
FDMMG	deep filtration, mixed media, gravity
FDMMP	deep filtration, mixed media, pressure
FDS	deep sand filter
FDSP	deep sand filter, pressure
FDW	deep walnut shell filter
FM-A	flash mixture - alum.
FLF	flocculation with ferric chloride
FLL	flocculation with lime
FLP	flocculation with polymer
FP	pressure filtration
HOD	hot oil decanter
N	neutralization
NA	neutralization with acid
NC	neutralization with caustic
NL	neutralization with lime
OWS	oil-water separator
PSP	primary scale pit
RC( )	recycle (percent)
SB	settling basin
SL	settling lagoon
SL-U	settling lagoon for underflow
ST-CL	scalping tank with chlorination
SS	surface skimmer
SSP	secondary scale pit
T	thickener
VF	vacuum filtration
VF-S	vacuum filtration of sludge

1.0 INTRODUCTION

Raw wastewaters from iron and steel manufacturing processes have been shown to contain potentially toxic pollutants [1]. Wastewater treatment techniques have been assessed for their effectiveness in removing identified and regulated pollutants from wastewaters generated by eight manufacturing process subcategories. The effectiveness of various treatment techniques in reducing biotoxicity has not been assessed, however. Outfall compliance data identify toxicities that persist, after currently applied treatments, in wastewaters from cokemaking, ironmaking, and steelmaking [2-12]. Available data for cold-forming effluents show low toxicity. No data are available for hot-coating and continuous coating effluents. Effluents from centralized treatment of combined wastewaters from several processes showed a range from an LC_{50} of 19.5 percent dilution to no mortality. (LC_{50} is the concentration, expressed as volume percent, lethal to 50 percent of the organisms.)

As part of the toxic pollutant control program, the U.S. Environmental Protection Agency is developing industry-specific toxicity information. This study develops data on wastewater toxicity, its treatability and its variability in treated effluent for eight iron and steelmaking subcategories: cokemaking, ironmaking, steelmaking, continuous coating, hot forming, pickling, cold forming, and hot coating. In addition, effluent data existing prior to the study are summarized.

2.0 SELECTION OF TREATMENT SYSTEMS FOR STUDY

Treatment technologies were selected and tested as parts of systems operated in seven different plants identified by letters A through G. Criteria applied in the selection of 24 systems for study were:

- Technologies representative to some extent of BPT, BAT, or NSPS systems [1]
- Toxic pollutants generated and wastewaters discharged
- Potential for treatment problems
- Steel production rate at test time reasonably representative.

Wastewater treatment systems in steel plants are each somewhat unique. While the 24 selected treatment systems offer many of the unit processes inherent in BPT and BAT models [1], a complete match, process by process, seldom exists. Systems selected do include unit processes that have been shown to decrease pollutant loadings.

One of the selected treatments systems for ironmaking represents BAT-4 technology, except for omission of dechlorination and final filtering. The system for suppressed combustion steelmaking was operated essentially as a BPT system. The wet combustion treatment system was BAT, except for moderate blowdown. One continuous casting system was BPT with addition of recycle; the other had blowdown from the scale pit to a municipal sewer. Plant A's hot strip mill treatment system lacked the filtration step of BPT, but used alternatives including flocculation with polymer and alum, and central treatment along with slabbing mill wastewaters. Plant D processed hot strip mill wastewater along with slabbing mill wastewaters, using filtration prior to discharge. Plant F used settling tanks for clarification, thus closely approximating BPT, then filtered the combined waters from the hot-strip, universal, and blowing mills. Plant B applied polymer treatment and oil skimming before directly discharging slabbing mill wastewaters.

The bar mill treatment system did not include filtration, but added flocculation and clarification, followed by recycle as does BAT-1.

Plant E's section mill wastewaters are treated by oil skimming, neutralization and flocculation with polymers before discharge.

Plant F's pickling treatment system is BPT, except that air flotation is lacking. Plant B combines pickling wastewaters with those from cold forming for treatment somewhat better than BPT-BAT-1.

Plant A combines cold rolling mill wastewaters with hot strip mill waters for treatment. Its tandem mill wastewater is processed in a central treatment system. Plant B's cold rolling wastewater treatment system is equivalent to BPT.

The hot coating system at Plant C resembles BPT without chromium reduction.

One central treatment system involves settling with chlorination and recycle. The other receives a more varied loading, requiring pretreatment for cyanide and chromium, followed by neutralization, flocculation with polymer, and clarification with skimming.

3.0 SAMPLING AND ANALYSIS

Sampling sites were selected upstream and downstream of treatment unit processes. Composite samples were obtained using Isco Model 2100 automatic samplers at all locations except those in designated hazardous areas. Composites in such areas were made from a corresponding set of grab samples. Composite sample increments were taken automatically every 15-30 minutes depending on the length of the sampling period, or by hand every 3 or 4 hours. Sampling periods for compositing were coordinated with production schedules. Thus, where 24-hour operation occurred (as in cokemaking, ironmaking, and steelmaking), sampling continued over that period. Where operation was limited in the number of turns (shifts) per week (as in many finishing operations), the sampling was similarly limited to avoid collection of wastewaters which were not receiving raw loadings from the production lines.

Sample containers were packed in coolers with ice. Bioassay samples were delivered immediately by the fastest possible means to EPA testing laboratories. Chemical analysis samples were transported, preserved with ice, under a chain of custody, and were analyzed within the prescribed limited holding periods [13]. To prevent losses of cyanide, volatile organics, and oil and grease through sample degradation that might occur during composite sampling, grab samples were taken for these constituents. Grab samples were also taken for onsite determination of pH, dissolved oxygen, and residual chlorine.

Table 3-1 identifies the methods of chemical analysis employed [13-16]. Test detection limits, standard deviations, and percent recovery are given in the references indicated. When limits had not previously been set, those obtained in this study are included.

During this study, 10 percent of the composite samples taken were split for chemical analysis by both laboratories for quality control purposes. The volatile organics and extractable organics analyses (Methods 624 and 625) yielded spectra which were screened for toxic and priority organics, pesticides, and PCB's, with detection limits typically less than 10 μg/L.

TABLE 3-1. METHODS OF ANALYSIS[a]

Constituent	Method number	Recovery %	Detection limit (μg/L)	Standard deviation (μg/L)
Antimony	204.2	NA[b]	3	NA
Arsenic	206.2	85-88	1	±9% R
Chromium	218.2	97-102	1	±0.8
Copper[c]	220.2	97	1	±3.8
Iron	236.1	1.8 B	30	±173
Lead	239.2	85-95	1	±3.7
Nickel[c]	249.2	100	1	±10
Selenium	270.2	94-112	2	14% R
Zinc	289.1	56.6 B	5	18
Total cyanide	335.2	85-102	20	±620
Ammonia	350.2	-5.5 B	50	±122
Fluoride	340.2	--	100	±30
Oil and grease	413.1	93	--	±900
pH	150.1	±0.16 unit	--	±0.12 unit
Phenolics (4AAP)	420.1	--	5	±4.2
Chlorine residual	330.3	--	1 mg/L	±0.09 mg/L
Total suspended solids	160.2	NA	NA	NA
Volatile organics	624	NA	10	NA
Extractable organics (base/neutral and acids)	625	NA	10	NA
Toxicological	--	--	--	--

R = Relative standard deviation.
B = Percent bias.
NA = Not applicable.

[a] Reference 16.
[b] Not available according to method.
[c] Limits from analysis of all samples during this study.

4.0 RESULTS AND DISCUSSION

Analytical results indicate that, in general, the wastewaters sampled are representative of their respective subcategories. While some raw wastewater values are markedly different from median values developed by EPA [1], the overall characterizations show typical subcategory trends. Results presented here, of course, represent only one 24-hour period, while subcategory data represent years of operation.

Bioassay result are summarized in Tables 4-1 and 4-2. Details of pollutant and toxicity reduction are discussed for each process subcategory. The tabulated results are limited to the regulated pollutants plus total organics and metals, compiled as the sum of all identified priority toxic pollutants.

4.1 COKEMAKING

Figure 4-1 indicates the succession of treatments and sampling points for the three cokemaking wastewater treatment systems studied.

Plant C treats combined flows of excess ammonia liquor from the free and fixed ammonia still, benzol plant wastewaters, and desulfurization wastewaters. The first two flows are continuous, under 24-hour operation, to the equalization tanks; the last flow is intermittent. Equalization tank holding capacity is 2,650 m^3. Influent to the biooxidation reactor (BOA-1) is drawn from the equalization tanks at a design rate of 1.14 m^3/min, first passed through a cooling tower, and diluted with river water at a design ratio of 75/300 by volume (75 m^3 of dilution water to 300 m^3 of wastewater). Phosphoric acid is added as a nutrient.

The BOA-1 has two basins, each with 136 submerged aerators. It was designed for single-stage parallel operation. Its effluent flows to clarifiers where solids separation is assisted by addition of polymer. The overflow is discharged to the river.

During the study, flow to the bioreactors was 0.83 m^3/min (73 percent of design). Coke production average 3,671 MTD (90 percent of rated capacity).

TABLE 4-1. BIOASSAY RESULTS, DAPHNIA

			Toxicity, EC_{50}	
			Raw wastewater	Treated wastewater
Cokemaking	BOA-1	C	0.4	1.5
	BOA-1	D	1.6	1.6 - 31
	Phys/Chem	G	2.1	5.3
Ironmaking		A	7.1	6.8
		D	55.2	42.1
Continuous Casting		B	100% killed 65%	100% killed 60%
		E	6.2	6.6
Hot Forming	Section		80% survived in 100%	60% survived in 100%
	Slab (B)		NT	NT
	Bar (A)		Could not calculate	Could not calculate
	Hot strip (F)		NT	NT
	Slab hot strip (A)[a]		NT	(Central tr)
	Bar (A)		Could not calculate	Could not calculate
Steelmaking	(Sup. Comb.)		--	58.6
	(Semi. Wet Open)		>16	<32
Hot Coating			4.1	100% survived in 100%
Central treatment[a]				<32
Pickling	Comb.		4.3	75% survived in 100%
	HCl		90% killed in 6.3	100% killed in 95% w.

NT = Nontoxic.

[a] To central treatment.

TABLE 4-2. BIOASSAY RESULTS, MINNNOWS

			Toxicity, LC_{50}	
			Raw wastewater	Treated wastewater
Cokemaking	BOA-1	C	0.61	3.8
	BOA-1	D	4.4	8.9
	Phys/Chem	G	0.85	71.5
Ironmaking		A	21.5	32.6
		D	22.6	NT[a]
Continuous Casting		B	NT	NT
		E	2.4	2.8
Hot Forming	(section)		NT	NT
	(slab), (bar)		NT	NT
	(hot strip)	F	NT	NT
	(hot strip)	D	NT	35.4 - NT
Central Treatment		A	--	NT
		E	2.4 - NT[b]	65% survived in 100%
Steelmaking	(Sup. Comb.)		--	71
	(Semi Wet Open)		NT	NT
Hot Coating			3.9	NT
Pickling	(comb)		6.9	NT
	(HCl)		8.8	NT

[a] NT = Nontoxic

[b] Range for different wastewaters treated.

	Plant		
	C	D	G
Ammonia still		s	
fixed	•	•	•
free	•s	•	•
Dephenolizer	•		•
Hot oil decanter			•s
Desulfurizer	•s		
Dissolved air flotation		•s	•s
Cooling tower	•s		
Light oil and final cooler condensate		•s	
Equalization	•		•s
Dilution	•		
BOA-1	•	•s	
Clarifier	•s		•s
Thickener		•s	
Filtration (Dual Med)			•s
Carbon ads.			•s
Alkaline chlorination			•s
Dilution			
Discharge	•	•	•

s = Sample point

Figure 4-1. Cokemaking.

Grab composite samples were taken representative of the excess ammonia liquor, the phenol plant wastewaters, the diluted feed to the bioreactors, and the clarifier effluent.

The toxicity reduction, shown in Table 4-3, through the BOA-1 and clarifiers (LC_{50}:0.61 to 3.8) for minnows is certainly statistically significant, when compared to the coefficients of variation for the test (37-93 percent). Nor could it have resulted from dilution alone. For dilution after the cooling tower, the ratio of LC_{50}'s would be no lower than 0.8, by:

$$\frac{V_1}{V_2} = \frac{LC_{50},\ 1}{LC_{50},\ 2} = \frac{1.14\ m^3/min}{1.42\ m^3/min} = 0.8 \quad .$$

The toxicity ratio is in fact 0.16 (0.61 ÷ 3.8).

The treated wastewater remained very toxic to minnows, even at final discharge. Several pollutants could have contributed to the toxicity. Table 4-4 shows water quality criteria and lethal limits which guide the assessment of sources of toxicity. By comparison, the treated effluent and the LC_{50} dilution exceeded these limits for ammonia, cyanide, and benzo(a)-pyrene. The increase in cyanide across the treatment systems is unusual. Biotreatment systems tend to remove free cyanide efficiently, except for complex metal cyanides [19].

Plant D collects only pretreated ammonia liquor in a holding tank of 757 m^3 capacity. This is fed at 45 m^3/h to the bioreactors, with light oil and final cooler condensate waters added on the way. Plant D's holding time is 14 hours; plant C's, 53 hours.

Plant D's bioreactor has four aeration cells, each with one surface aerator. The total aeration (air flow) rate was 142 kg/h (it was 12,270 kg/h at Plant C). Retention time in the reactor was 32 hours. Phosphoric acid was added as a nutrient, and bay water was added to dilute the wastewater (up to 25 percent) and lower the thiocyanate concentration.

Overflow from the final thickener was discharged to receiving waters; sludge was recycled to the aeration tanks.

Samples were taken of the raw ammonia liquor, the light-oil condensate, the final cooler condensate, the mixed feed to the BOA-1, and the thickener effluent.

TABLE 4-3. COKEMAKING: POLLUTANT REDUCTION, PLANT C

Component	Units	ASFF;DS;DP ;		E ;	CT;Dilution:BOA-1;CL	Percent reduction
		Δ	Δ	Δ	Δ	
Flow	m^3/min			0.83	1.1	
pH	S.U.	10	5	9	7.8	
Ammonia	mg/L	1,420	67.5	1,002	612[a]	(39)
Oil and grease	mg/L	14.4	10.85	26.3	6.4	(76)
Phenol (4AAP)	mg/L	1,060	50.8	831	0.23	(99.9)
Residual chlorine	mg/L					
Total suspended solids	mg/L	28	<2	80	216	-
Benzene	μg/L	4.2	58,500	11,600		
Naphthalene	μg/L	-	9,500	783	<2	99.7
Benzo(a)pyrene	μg/L	-	-	ND	136[a]	-
Tetrachloroethylene	μg/L	-	-	-	-	-
Cyanide	mg/L	-	-	<0.02	20.2[a]	-
Total organics	μg/L	-	-	73,233	916	99.9
Lead	μg/L	-	-	-	-	-
Nickel	μg/L					
Zinc	μg/L	1,910	500	650	310[a]	52.3
Total metals	μg/L	4,294	804	2,694	1,679	38
Toxicity, minnow, 96 h	LC_{50}	0.61	0.61		3.8	
Toxicity, daphnia, 48 h	LC_{50}	0.4	<1.0		1.5	

[a] Exceeds toxicity limits, Table 4-4.

TABLE 4-4. WATER QUALITY CRITERIA AND TOXICITY LIMITS

Pollutant	Limits	
	Criteria[a]	Toxicity[b]
Ammonia, mg/L	0.4 - 10.5[c] (0.09 - 2.24)[d]	0.1 - 2
Arsenic, mg/L	0.14 (0.072)	17.8
Cadmium, μg/L	2 - 10	300
Chromium, trivalent, μg/L	870 - 2,700 (42 - 130)	--
Copper, μg/L	8.4 - 29 (5.8 - 20)	20 - 180
Lead, μg/L	25 - 160 (1 - 64)	330 - 2,500
Nickel, μg/L	56 - 96[e]	100 - 1,000
Zinc, μg/L	47[e]	300 - 500
Cyanide, μg/L	22	40 - 100[f]
Chlorine, μg/L	14 (8.3)	30 - 1,500[g]
Phenols, μg/L	500[e]	1,000 - 2,000
Benzene, μg/L	478[h]	
Benzo(a)pyrene, μg/L	0.028[h]	
Naphthalene, μg/L	--	620[i]
Tetrachloroethylene, μg/L	8[h]	

[a] Maximum conc., EPA, published in Federal Register 49, 26, February 7, 1984, 4551-4554.

[b] Lowest conc. at which toxicity to minnows has been found [17].

[c] Range depends on pH for ammonia; on hardness for others.

[d] Thirty-day average, or limit other than maximum, in parentheses.

[e] Prior standard.

[f] Dodge and Reams [18].

[g] Varies with species.

[h] To limit risk of cancer.

[i] Effluent guidelines.

During the tests several upsets in operation of the system occurred. In the first hours, the holding tank was bypassed, and ammonia liquor after distillation was fed directly to the BOA-1. No waste was fed from the light-oil sump. At midnight of the 24-hour test, the holding tank was allowed to overflow to the BOA-1, carrying over accumulated lime solids. A high pH developed in the BOA-1, and bioreactivity was affected adversely. The data reflect these upsets. The bioassay only was repeated at a later date when these upsets did not occur.

During the study, flow to the BOA-1 was approximately 1.0 m^3/min (70% of design). Coke production was 2,120 MTD (70% of capacity).

Table 4-5 shows the higher biotoxicities obtained during the upsets. As might be expected from the shorter treatment times and upsets, phenol reduction is only 25%, compared to 99.9% for Plant C. Here again cyanide removal is not estimable. Ammonia removal is higher than for Plant C (78% vs. 39%).

The remaining toxicity of the treated effluent coincides with concentrations of ammonia, phenol, benzo(a)pyrene, cyanide, and zinc that exceeded toxic limits.

Plant G uses a physical/chemical treatment system. Wastewaters were fed to an equalization tank from four sources: the hot oil decanter, the phenolate storage area, the light-oil separator and the final cooler. The phenolate wastewaters passed through a free ammonia still, a dephenolyzer, and a fixed ammonia still prior to mixing for equalization. The succession of treatments applied thereafter were: clarification, filtration, carbon adsorption, and alkaline chlorination. By adsorbing organics prior to chlorination, formation of chlorinated organics is avoided. Also, if toxics break through from the adsorbers, they can be subsequently chlorinated.

During the study, flow through the equalization tank was 0.67 m^3/min (52% of design). Detention (holding) time was 24 hours. At this flow, other important process parameters differed from design, as follows:

TABLE 4-5. COKEMAKING: POLLUTANT REDUCTION PLANT D

Component	Units	Light oil + final cooler condensate ↓ Δ	Raw NH_3 Liquor → Δ	ASFF-L → ; E; ↓ Δ	BOA-1; T Δ	Percent reduction
Flow	m^3/min	--		1.0	0.9-1.25	
pH	S.U.	8.0	9.1	11.9	12.2	
Ammonia	mg/L	119	2,710	107	22.7[a]	78
Oil and grease	mg/L	235	80.2	11.1	14.6	-
Phenol (4AAP)	mg/L	48.9	589	149	111[a]	25
Residual chlorine	mg/L	-	-	-	-	-
Total suspended solids	mg/L	19	66	1,040	529	49
Benzene	μg/L	286,000	8,950	3,570	212	94
Naphthalene	μg/L	56,300	56,000	4,130	392	90.5
Benzo(a)pyrene	μg/L	ND	ND	<10	<10[a]	-
Tetrachloroethylene	μg/L	-	-			
Cyanide	mg/L	<0.02	<0.02	0.1	0.46[a]	-
Total organics	μg/L	446,971	483,817	129,867	80,326	38
Lead	μg/L	-	-	-	-	
Nickel	μg/L	-	-	-	-	
Zinc	μg/L	640	120	240	110[a]	54
Total metals	μg/L	683	1,214	899	810	9.9
Toxicity, minnow, 96 h	LC_{50}		0.17	4.42	8.84[b]	
Toxicity, daphnia, 48 h	EC_{50}		0.16	1.6	<1.6[c]	

ND = None detected.

[a] Exceeds toxicity limits or criteria.

[b] 32.3 on resample.

[c] 31 on resample.

		Value	
Treatment unit	Parameter	Design	Test
Clarifier	Overflow, $m^3/(m^2 \times min)$	0.0072	0.0037
Filter	Flow-through rate, $m^3/(m^2 \times min)$	0.09	0.045
Adsorber	Flow-through rate, $m^3/(m^2 \times min)$	0.18	0.09
Chlorinator	Detention time, h	1.5	2.8

Samples were taken before and after dissolved air flotation (hot-oil decanter wastewater), after equalization, after clarification, after filtration, after carbon adsorption, and after the alkaline chlorination.

Table 4-6 shows an LC_{50} for minnows of 71.5%, and the reduction of ammonia and phenols to below detection limits. Priority pollutants were reduced 99.9% to a residual 30 µg/L. Residual chlorine in the effluent exceeded toxic limits (9,100 µg/L vs. 1,500). Cyanides, although reduced 87%, remained above toxic limits at the LC_{50} dilution, and copper, at 3,460 µg/L, also exceeded toxic limits. The buildup of concentration of this metal across the adsorber was confirmed by subsequent sampling and testing by four different laboratories. The presence of phenols (4AAP) after the adsorber was not confirmed by the results of GC/MS analyses. In resamples, the phenol concentration was much lower (34 µg/L by AAP) and was consistent with the GC/MS results (Table 4-7).

Tests made by the four laboratories, shown in Table 4-7, do not check as well as those made under the QA plan. The larger differences are due to lack of uniformity in the methods used, e.g., three of the phenol results shown were obtained by the 4AAP method; one is by GC/MS.

Conclusions

The physical-chemical treatment system reduced biotoxicity much more than did the biosystems.

The physical-chemical treatment effected greater reduction of zinc, but showed copper buildup across the adsorber which apparently formed complex metal cyanides that resisted chlorination.

Causes to toxicity after biotreatment appear to be insufficient removal of ammonia, benzo(a)pyrene, phenols, cyanides and zinc. Causes after physical/

TABLE 4-6. COKEMAKING: POLLUTANT REDUCTION, PLANT G

Component	Units	HOD; Δ	ASFF;DP; → AF → Δ	E ; Δ	CL ; FDMMP Δ	; Δ	CAG ; CLA Δ	Δ	Percent reduction
Flow	m^3/min	0.08	0.08	0.67	0.67	0.67	0.67	0.69	
pH	S.U.	6.8	6.6	8.4	8.4	8.2	8.4	8.8	
Ammonia	mg/L	1.4	1.4	17	16.7 (2)[a]	16.8 (2)	16.8 (2)	ND	99
Oil and grease	mg/L	-	12.6	1.37	28.9 (-2,000)	15.4 (48)	ND (>99)	8.8	70
Phenol (4AAP)	mg/L	87	745	390	601 (-54)	82 (86)	22 (95)	ND	>99
Residual chlorine	mg/L	-	-	-	-	-	-	9.1[c]	-
Total suspended solids	mg/L	21	2	159	107 (33)	33 (79)	5 (97)	16	90
Benzene	µg/L	880	1,200	18,000	15,000 (17)	9,000 (50)	BDL[b]	BDL	100
Naphthalene	µg/L	1,200	720	250	1,700 (-580)	1,100 (35)	BDL (98)	BDL	98
Benzo(a)pyrene	µg/L	-	-	-	-	ND	ND	ND	-
Tetrachloroethylene	µg/L	-	-	-	-	ND	ND	ND	-
Benzo(a)anthracene	µg/L	BDL	BDL	24	14 (41)	BDL	BDL	BDL	(>60)
Cyanide	mg/L	0.07	0.066	54.2	44.0 (19)	43.3 (20)	31.2 (42)	6.8[c]	(87)
Total organics	µg/L	13,085	13,445	32,333	26,873	19,034	BDL	30	99.9
Lead	µg/L	16.7	2.9	19	16.7 (12)	ND (>99)	9.2 (51)	9.2	51
Nickel	µg/L	ND	ND	35.2	29.2 (17)	13.3 (62)	32.1 (9)	37.2	-6
Zinc	µg/L	39	22	870	107 (87)	72 (92)	15 (98)	17	98
Total metals	µg/L	70.6	27	1,499	591	414	3,800	3,841[c]	-156
Toxicity, minnow, 96 h	LC_{50}	12.5	25	0.85	0.72	0.67	1.0	71.5	
Toxicity, daphnia, 48 h	EC_{50}	-	50	60% survived in 5%	75% survived in 2%			5.3	
24 h		2.1				1.3	1.5		

ND = None detected.

BDL = Below detection limits.

[a] Values are cumulative % reduction across the intermediate processes.

[b] <10 µg/L.

[c] Exceeds toxicity limits, Table 4-4.

TABLE 4-7. COKEMAKING: COMPARATIVE TESTS OF RESAMPLES PHYSICAL CHEMICAL SYSTEM

Component analyst	Hot-oil decanter	Air flotation	E	CL	FDMMP	CAG	CLA
Phenols mg/L							
RTI	59.7	48.8	82.8	79.6	75	<.05	<.05
S[a]	55	42	75	80	75	0.015	0.02
Mead	60	40	80	80	80	0.3	<.01
Plant G	53.9	42.7	72.6	70.2	64.7	0.034	0.017
Copper µg/L							
RTI	68.2	7.5	534	315	104	4,604	2,424
S	<50	<50	300	150	50	1,700	2,000
Mead	<100	<100	230	<100	<100	940	1,000
Lead µg/L							
RTI	5.7	ND	ND	ND	6.2	3.8	5.8
S	--	55	100	--	--	--	<50
Mead	<200	<200	<200	<200	<200	<200	<200
Nickel µg/L							
RTI	2.7	39.7	29.1	39.7	18.5	18.5	44.9
S					0 to <50		
Mead					<100		
Iron mg/L							
RTI	0.68	0.85	22.6	3.6	2.4	3.9	3.9
S	0.55	0.75	2.5	3.6	2.5	3.6	3.8
Mead	0.48	0.55	2	2.3	1.8	2.7	2.9

ND = None detected.

[a] S = Supplier of carbon.

chemical treatment appear to be insufficient removal of residual chlorine, extraneous copper, and cyanides.

Cyanide removal in both systems was apparently constrained by the presence of complex metal cyanides. One reason for low effluent cyanides from the biosystems is the low influent concentration.

4.2 IRONMAKING

Figure 4-2 shows the wastewater treatments and sampling points for the two plants studied (A and D).

Plant A recycles 96% of the treated water and quenches slag with the blowdown. Spent scrubber water flows via a splitter box to two thickeners. Upstream of the box, anionic polymer assists in settling the carbon particulates. At the splitter box, cationic polymer is added to improve settling of solids in the thickeners. Sludge from the thickeners is recycled until the solids become 10-15% by volume, whereupon the sludge is hauled by truck to landfill.

During the study, flow through each thickener was 15 m^3/min (holding time, 3.6 h).

Waters flow from the thickeners to a hot well, thence to a cooling tower where makeup water is added as required. Blowdown, from the hot well, was 1.1 m^3/min. This was sent through a surge tank to a clarifier with a capacity of 946 m^3 (holding time, 14 h). Clarified water passed to chlorinators, pH was adjusted with lime, and the waters were chlorinated to breakthrough.

Samples were taken at the splitter box, after the thickener, and after the chlorinator. Analyses are given in Table 4-8.

Toxicities for minnows and daphnia were not significantly different in the raw wastewaters and the final effluent, although 99% of the organics and metals were removed. Raw waters exceeded toxic concentration limits for ammonia and zinc, while final effluent waters exceeded limits for chlorine and zinc. Since the metals would be mostly in particulate form, the excess chlorine is the likely factor in final effluent toxicity.

Plant D uses a once-through treatment system. Scrubber waters, slag pit waters, and dekishing station wastewaters flow to a flocculation tank of 341 m^3 capacity. During the study, flow was 56.8 m^3/min (79% of design) equivalent to a holding time of 6 min. Production was 6,350 MTD (64% of capacity for four blast furnaces).

	Plant	
	A	**D**
Primary scale pit	•	•s
Splitter box	•s	Dekishing wastewater
Flocculation with polymer	•	•s
Thickener	•s	•s
Cooling tower	•	
Recycle	•(96%)	
Blowdown to		
Clarifier	•	
Alkaline chlorination	•s	
To quench	•	
Discharge		•

s = Sample point

Figure 4-2. Ironmaking—wastewater treatments and sampling.

TABLE 4-8. IRONMAKING: POLLUTANT REDUCTION, PLANT A

Component	Units	Feed; Splitter Δ	FLP; T; CT; RC(96) → CL; Δ	CLA → Quench Δ	Percent reduction
Flow	m^3/min	30.3	30.3	1.1	
pH	S.U.	7.1	7.0	7.6	
Ammonia	mg/L	79	57.8 (27)[a,b]	<0.4	99.5
Oil and grease	mg/L	9.5	2.7 (71)	5.6	41
Phenol (4AAP)	mg/L	0.25	<0.06 (76)	<0.06	76
Residual chlorine	mg/L			26.5[b]	
Total suspended solids	mg/L	9,604	29 (99.7)	203	97.9
Benzene	µg/L	ND	ND	ND	--
Naphthalene	µg/L	10	ND	ND	99
Benzo(a)pyrene	µg/L	ND	ND	ND	--
Tetrachloroethylene	µg/L	ND	ND	ND	--
Cyanide	mg/L	c	0.042	<0.02	52.4
Total organics	µg/L	23	ND	ND	99
Lead	µg/L	73,967	533 (99.3)	32.8	99.9
Nickel	µg/L	119	20.5 (83)	<19	84
Zinc	µg/L	349,340	24,790 (93)[b]	4,100[b]	98.8
Total metals	µg/L	427,833	25,384 (94)	4,172	99
Toxicity, minnow (96 h)	LC_{50}	21.5	18.4	22.6	
Toxicity, daphnia (48 h)	EC_{50}	7.1	5.1	6.8	

ND = None detected.

[a] Values in parentheses are cumulative percent reduction.

[b] Exceeds toxicity limits, Table 4-4.

[c] Not quantified due to sample turbidity.

Overflow from flocculation was fed to a 48 m dia. thickener (surface area: 1,867 m^2, depth 6.1 m). Overflow rate was 0.030 $m^3/m^2 \times$ min, vs a design rate of 0.041. Polymer was added to the thickener to aid settling. Underflow from the thickener passed through vacuum filters. The solids were stored for future processing. Overflow from the thickeners is discharged to receiving waters.

Samples were taken of the separate dekishing wastewater, the combined waters into the flocculation tank, and the overflow from the thickener.

Table 4-9 shows no toxicity to minnows for the raw waters or the treated effluent. Ammonia exceeded slightly the toxic limits, and zinc exceeded limits in the raw waters. These may account for the toxicity shown in the daphnia.

Conclusions

Blast furnace waters tested were nontoxic to minnows when the total metals concentration was below 2,000 µg/L.

These wastewaters were more toxic to daphnia than to minnows.

Excess chlorine contributed to the toxicity of the final effluent so treated.

4.3 STEELMAKING

Figure 4-3 shows the wastewater treatments and sampling points for the two plants studied (suppressed combustion and wet open combustion at Plant A).

The Suppressed Combustion treatment system had no blowdown during the study because of the extent of evaporative loss in the quencher. Water from the venturi scrubbers passed to the quenching tank, was used in the quench circuit, and then returned through hydroclones and classifiers, along with water from a secondary ventilation scrubber, to a "distribution box" where polymer was added to induce settling in the two following thickeners. Flow rates were 11.4 m^3/min from the classifiers and 3.7 m^3/min from the secondary ventilation system. Holding time was 6.6 h vs. a design value of 5.0 h.

Thickener overflow was sent to a holding tank, from which it is usually recycled with a 5% blowdown. Thickener underflow passed to a sludge holding tank.

TABLE 4-9. IRONMAKING: POLLUTANT REDUCTION, PLANT D

Component	Units	PSP ———	——— FLP;	T	Percent reduction
		Dekishing water	Δ		
Flow	m^3/min	1.7	56.8	56.8	
pH	S.U.	12	7.1	6.9	
Ammonia	mg/L	2.6	5.5	3.6[a]	35
Oil and grease	mg/L	8.2	4.2	2.2	47.6
Phenol (4AAP)	mg/L	0.09	0.12	0.07	41.7
Residual chlorine	mg/L		<0.02	<0.02	--
Total suspended solids	mg/L	133	847	38	95.5
Benzene	μg/L	ND	ND	ND	
Naphthalene	μg/L	ND	ND	ND	
Benzo(a)pyrene	μg/L	ND	ND	ND	
Tetrachloroethylene	μg/L	ND	ND	ND	
Cyanide	mg/L	<0.02	<0.02	0.05	
Total organics	μg/L	ND	ND	ND	
Lead	μg/L	<1.9	329	61.2	81.4
Nickel	μg/L	174	193	13	93.3
Zinc	μg/L	<30	1,570[a]	300	80.9
Total metals	μg/L	291	2,164	380	82.4
Toxicity, minnow, 96 h	LC_{50}		100% survival in 100%	100% survival in 100%	
Toxicity, daphnia, 48 h	EC_{50}		55.2	42.1	

ND = None detected.

[a] Exceeds toxicity limits, Table 4-4.

	Suppressed Combustion	Semi-Wet Open
Classifier	• s	Surge Tank
Secondary vent	• s	s
Flocculation with polymer	• s	• s
Thickener	• s	•
Acidification	•	• s
Recycle	• (100%)[a]	•
Blowdown to Clarifier	•	
Discharge	•	•

s = Sample point
a = Actual value, design value = 95%

Figure 4-3. Steelmaking--wastewater treatments and sampling.

Production was 1,950 MTD (72% of capacity).

Sampling was conducted from 11 p.m. to 7 a.m. on successive days. Samples were taken from the classifier inlet (quencher water), from the secondary vent return, and from the holding tank before recycle. The inlet to the thickeners was calculated from the results of the first two samples.

Table 4-10 shows low remaining toxicity for both minnnows and daphnia. The residual toxicity appears to be related to the levels of phenol, lead, and zinc, all of which are above some of the limits of Table 4-4. The ammonia level at 0.4 mg/L cannot be discounted as a possible contributor to toxicity at the pH values shown.

The Wet Open Combustion system collects waters from the scrubbers in a surge tank and passes them to one of two thickeners, adding polymer to aid settling. The thickener effluent is pH adjusted with sulfuric acid, passed to a holding tank, and recycled, with blowdown to a second thickener, which also receives water from the process spark box. Blowdown and spark-box waters are sewered after passing through this thickener. Makup water is added at the scrubbers. Sludges from both thickeners are landfilled.

Production was 9,253 MTD (73% of capacity). Wastewater flow was at the full 22.7 m^3/min rate. Holding time in the main thickener was thus 1.2 h; in the blowdown thickener, 10 h.

Samples were taken at the surge tank, the influent to the blowdown thickener, and at the effluent from this thickener.

Table 4-11 shows that the minnows survived in 64% wastewater, treated or untreated. Had stronger dilutions been tested, they would, perhaps, have yielded LC_{50} values close to the 71 obtained for the suppressed combustion system. The toxicity to daphnia may relate to concentrations of lead and zinc, which exceeded limits. Ammonia is within the toxic range for the pH given.

Conclusions

Steelmaking raw wastewaters were moderately toxic, and so were the treated wastewaters. The simple flocculation and clarification treatments removed 97-99% of the metals. Remaining concentrations of lead and zinc are within the toxic range for daphnia as was the concentration of ammonia.

TABLE 4-10. STEELMAKING, SUPPRESSED COMBUSTION: POLLUTANT REDUCTION, PLANT A

Component	Units	Classifier Δ	Secondary vent Δ	Δ[a]	FLP; T; RC; CL Δ	Percent reduction
Flow	m^3/min	11.4	3.7	15.1	15.1	
pH	S.U.	12.4	--		11.6	
Ammonia	mg/L	1	0.8	0.95	0.4	
Oil and grease	mg/L	10.9	6.5	9.8	5.1	
Phenol (4AAP)	mg/L	0.52	0.79	0.59	0.6[b]	
Residual chlorine	mg/L	<0.2	--		<0.2	
Total suspended solids	mg/L	9,644	931	7,509	73	
Benzene	μg/L	ND	4.5	1.1	ND	99
Naphthalene	μg/L	ND	4.4	1.07	2	--
Benzo(a)pyrene	μg/L	ND	ND		ND	
Tetrachloroethylene	μg/L	ND	ND		ND	
Cyanide	mg/L	<0.02	<0.02	<0.02	<0.02	
Total organics	μg/L	ND	8.9	2.2	2	9
Lead	μg/L	102,000	8,240	79,026	811[b]	99
Nickel	μg/L	4,180	1,280	3,469	6	99.8
Zinc	μg/L	194,000	23,200	152,148	852[b]	99.4
Total metals	μg/L	304,424	33,582	238,059	1,700	99.3
Toxicity, minnow (96 h)	LC_{50}		Sample lost lab accident		71	
Toxicity, daphnia (48 h)	EC_{50}		Sample lost lab accident		58.6	

ND = None detected.

[a] Constructed from classifier and secondary vent.

[b] Exceeds toxicity limits.

TABLE 4-11. STEELMAKING: SEMI-WET OPEN, PLANT A

Component	Units	Scrubber surge tank Δ	Δ	FLP;	T;	A; Δ	RC	Percent reduction
Flow	m^3/min	--	22.7			22.7		
pH	S.U.	10.3	10.9			9.3		
Ammonia	mg/L	1.7	0.5			0.6^a		
Oil and grease	mg/L	3.1	3.1			5.6		
Phenol (4AAP)	mg/L	<0.06	<0.06			<0.06		
Residual chlorine	mg/L	ND	ND			ND		
Total suspended solids	mg/L	1,894	1,302			19.5		98.5
Benzene	μg/L	ND	ND			ND		
Naphthalene	μg/L	ND	ND			ND		
Benzo(a)pyrene	μg/L	ND	ND			ND		
Tetrachloroethylene	μg/L	ND	ND			ND		
Cyanide	mg/L	<0.02	<0.02			<0.02		
Total organics	μg/L	ND	ND			ND		
Lead	μg/L	10,147	$2{,}589^a$			191.4^a		93
Nickel	μg/L	178	50.4			<19		62
Zinc	μg/L	158,110	57,950			$1{,}430^a$		98
Total metals	μg/L	159,500	61,059			1,666		97.3
Toxicity, minnow (96 h)	LC_{50}	100% survival in 64%	100% survival in 64%			100% survival in 64%		
Toxicity, daphnia (48 h)	EC_{50}	>16	>16			>32		

ND = None detected.

[a] Exceeds toxicity limits.

4.4 CONTINUOUS CASTING

Figure 4-4 shows the wastewater treatment systems and sampling points for the two plants studied (Plants B and E).

Plant B's system passed machine cooling water, which is also used for direct spraying of the strand of steel below the mold to a scale pit for removal of heavy scale and oil. The water flowed from the scale pit through two deep bed filters of walnut shells operated in parallel, and to a cooling tower from which, after addition of makeup water, it was recycled. Blowdown from the scale pit and filter backwash were discharged to the slabbing mill stream.

Production was 789 MT per turn during the tests (42% of rate capacity). Wastewater flow was at the normal 13.25 m^3/min.

Samples were taken (only during active production) after the scale pit and surface skimmer, and after filtration.

Table 4-12 shows that the raw and treated waters were nontoxic to minnows, and that all pollutants were at relatively low concentration. The toxicity to daphnia (100% waste killed 60%) may have been due to the zinc levels, or the oil and grease.

Plant E requested that descriptions of its wastewater treatment system supplied for this study be treated as confidential. Therefore, the unit operations studied are identified from published sources [1], and only the analytical data obtained in this study are presented. The wastewaters pass through a scale pit, a deep sand filter, a cooling tower, and are then recycled. Blowdown is from the scale pit.

Samples were taken after the scale pit and after filtration. Flows were at normal rates. Production was an estimated two-thirds of normal.

Table 4-13 shows high toxicity to both organisms, in both raw and treated waters. Nickel, zinc, and copper (at 47.9 µg/L) all exceeded toxic limits in the samples of raw and treated waters.

Conclusions

Continuous casting wastewaters studied herein contained no toxic levels of organics, ammonia, phenols, or cyanides. Treatment consisted of filtration, after preliminary settling and removal of debris. The resulting biotoxicity varied as the residual concentration of metals from very low to very high.

	Plant	
	B	E
Primary scale pit	•	•
Surface skimmer	• s	• s
Deep filter	• s (walnut shell)	• s (sand)
Cooling tower	•	• s
Recycle	•	•

s = Sample point

Figure 4-4. Continuous casting—treatments and sampling.

TABLE 4-12. CONTINUOUS CASTING: POLLUTANT REDUCTION, PLANT B

Component	Units	PSP; SS; Δ	FDW; Δ	CT: RC	Percent reduction
Flow	m^3/min	13.25	13.25		
pH	S.U.	6.0	5.0		
Ammonia	mg/L	<0.4	<0.4		
Oil and grease	mg/L	25.7	27.7		
Phenol (4AAP)	mg/L	0.05	<0.02		76
Residual chlorine	mg/L	<0.2	<0.2		
Total suspended solids	mg/L	29	30		
Benzene	µg/L	ND	ND		
Naphthalene	µg/L	ND	ND		
Benzo(a)pyrene	µg/L	ND	ND		
Tetrachloroethylene	µg/L	ND	ND		
Cyanide	mg/L	<0.02	<0.02		
Total organics	µg/L	ND	ND		
Lead	µg/L	8.0	6.5		18.8
Nickel	µg/L	<4.6	<4.6		
Zinc	µg/L	96	66[a]		31.3
Total metals	µg/L	157.8	117.2		26
Toxicity, minnow (96 h)	LC_{50}	100% survival in 100% waste	100% survival in 100% waste		
Toxicity, daphnia (48 h)	EC_{50}	100% waste killed 65%	100% waste killed 60%		

ND = None detected.

[a] Exceeds toxicity limits, Table 4-4.

TABLE 4-13. CONTINUOUS CASTING: POLLUTANT REDUCTION, PLANT E

Component	Units	PSP;	↑ SS; Δ	FDS ; Δ	RC	Percent reduction
Flow	m^3/min		2.27	2.27		
pH	S.U.		7.8	7.7		
Ammonia	mg/L		2.3	<0.4		83
Oil and grease	mg/L		<1.0	<1.0		--
Phenol (4AAP)	mg/L		0.03	0.03		--
Residual chlorine	mg/L		<0.2	<0.2		
Total suspended solids	mg/L		77	10		87
Benzene	μg/L		ND	ND		
Naphthalene	μg/L		ND	ND		
Benzo(a)pyrene	μg/L		ND	ND		
Tetrachloroethylene	μg/L		ND	ND		
Cyanide	mg/L		<0.02	<0.02		0
Total organics	μg/L		ND	ND		
Lead	μg/L		5.4	5.4		0
Nickel	μg/L		1,280[a]	1,190[a]		7
Zinc	μg/L		360[a]	300[a]		17
Total metals	μg/L		4,950[a]	4,885[a]		1.2
Toxicity, minnow (96 h)	LC_{50}		2.4	2.75		
Toxicity, daphnia (48 h)	EC_{50}		6.2	6.6		

ND = Not detected.

[a] Exceeds toxicity limits, Table 4-4.

Metals removal by the treatments was low (17-26%). The high toxicity at Plant E may possibly have been due, in part, to the addition of biocides, corrosion inhibitors, or dispersants that were not detected in the analysis. However, at Plant E, nickel, zinc, and copper all exceeded toxic limits.

4.5 HOT STRIP AND COLD ROLLING MILLS

Figure 4-5 shows the treatment systems studied at three plants. Plant A's system also handles cold rolling. Waters flow from roughing and finishing stands, runout tables and coilers to scale pits with oil skimmers. The flow continues to a "flash mixing tank" where the streams are mixed with cold rolling waters and treated with alum and polymer, then pumped to parallel clarifiers. Retention time therein was 1.6 h (90% of design) at the 75.3 m^3/min flow rate during the study. Overflow from the clarifiers was mixed with hot strip mill noncontact cooling waters, the rest of the wastewaters from the scale pits, and slabbing mill wastewaters. The final combined streams went to central treatment.

Central treatment included scalping tanks with chlorination, cooling towers, and settling basins. Total flow-through was an estimated 568 m^3/min. Equivalent holding time in the scalping tanks was 5 min; in the settling basins, 1.4 h. Water from the settling basins is recycled to several mills.

Samples were taken after the scale pit for the finishing strand and run-out table waters; after the cold rolling mill sump, and its scalping pit; after the clarifier for the combined waters; and after the settling basins for central treatment.

Table 4-14 provides a basis for several comparisons, none involving just hot forming or just cold rolling. Minnows survived in 64% raw wastewaters of the scale pit, which were only from hot forming. Daphnia showed an EC_{50} of >32%. Grab samples from other pits showed similar chemical content but were not tested by bioassay. Residual chlorine may have contributed to the observed toxicity.

The cold rolling raw wastewater was more toxic, with a minnow LC_{50} of 45 and a daphnia EC_{50} of 8.3. This sample showed much more oil and grease, and concentrations of lead, nickel, and zinc exceeded limits. Further increase in toxicity after the cold rolling scalping relates to the combining of the sump waters with water from another cold rolling mill. The latter is the source of

	Plant		
	A	D	F
Primary scale pit(s)	●s	●s(three)	●s(two)
Settling basin			●
Surface skimmer	●s	●	●
Cold rolling mill; sump and sealing pit	s		
Flocculation with polymer	●s		
Flocculation with aluminum	●		
Clarifier	●s		
Surface skimmer	●		
Other wastewaters added	●		
Scalp tank with chlorination	●		
Cooling tower	●		
Settling basin	●s		●s
Recycle	●		
Filtration		●FDMMP_s	●FDSP_s
Discharge		●	●

s = Sample point

Figure 4-5. Hot forming hot-strip mills—treatments and sampling.

TABLE 4-14. HOT FORMING, HOT STRIP, COLD ROLLING: POLLUTANT REDUCTION, PLANT A

Component	Units	Scale pit 3^a ;	Cold roll sump ;	Cold roll scalp →	FLP;FLA;	Other wastewater ↓ CL;CNT;SS	SB;RC	Percent reduction[d]
Flow	m^3/min	75.7	0.15	2.3	78	78^b	416	
pH	S.U.	7.7	7.7	5.6		7.5	7.7	
Ammonia	mg/L	<0.4	-	-		1.2	<0.4	
Oil and grease	mg/L	<0.4	8,109	5,158	153 (88)	18	17.8	88.4
Phenol (4AAP)	mg/L	<0.06	-	-		<0.06	<0.06	
Residual chlorine	mg/L	<0.2	-			<0.2	0.2	
Total suspended solids	mg/L	54	203	209	58.9	16 (73)	9	84.7
Benzene	μg/L	ND	ND	ND		ND	ND	
Naphthalene	μg/L	ND	ND	ND		ND	ND	
Benzo(a)pyrene	μg/L	ND	ND	ND		ND	ND	
Tetrachloroethylene	μg/L	ND	ND	62.7		ND	ND	
Cyanide	mg/L	<0.02	-	-		<0.02	<0.02	
Total organics	μg/L	ND	ND	79.7		ND	ND	
Lead	μg/L	17.9	41^c	596^c	35	12.2 (65)	13	63
Nickel	μg/L	<19	82^c	272^c	25.6	24 (6)	<19	26
Zinc	μg/L	<28	52^c	170^c	32.3	<28 (13)	<28	13
Total metals	μg/L	105	602	2,376	173	96.5 (44)	123	29
Toxicity, minnow, 96 h	LC_{50}	100 % survived in 64%	45	17.7	-	100% survived in 64%	100% survived in 64%	
Toxicity, daphnia, 48 h	EC_{50}	>32	8.3	<1.0	-	>32	>32	

ND = None detected.

[a] Wastewaters from finishing stands and runout tables.

[b] Estimates for combined wastewaters subjected to subsequent treatments.

[c] Exceeded toxicity limits, Table 4-4.

[d] Dilution accounts for part of the reduction.

tetrachloroethylene and of increased lead, nickel, and zinc loadings, all of which may have contributed to the toxicity.

The combined wastewater toxicity was reduced substantially after passage through the clarifiers, partly due to dilution, since the hot-forming wastewater, at 75.7 m^3/min, was 31 times the sum of the other sources.

Central treatment applied to these plus other wastewaters did not alter the toxicity beyond the limits of test precision.

Plant D collects hot forming wastewaters in scale pits: two for the roughing stand; one for the finishing stand, mill run-out tables and coilers; one for the slabber and scarfer. These were combined for treatment with those from hot forming. Oil was removed at the finishing stand scale pit. Combined waters were filtered using sand and anthracite coal. The filtrate was discharged to receiving waters.

During the study, total flow to the filters was 102 m^3/min. Total filter surface area was 291 m^2. The filtration rate was slightly below the design rate of 0.5 $m^3/min \times m^2$. Production was 6,532 MTD (normal capacity).

Samples were taken after the slabber scale pit, after the finish stand scale pit, after the roughing stand scale pit, and after filtration.

Table 4-15 shows the slabber and finish stand wastewaters to be nontoxic to minnows. The LC_{50} was 35.4 for filtered waters, which included an additional waste stream. This stream was not separately tested for biotoxicity. Ammonia, nickel, or zinc may have contributed to the toxicity. A repeat sample showed 100% survival, but metals and ammonia were not determined.

Plant F collected wastewaters from its universal mill (roughing stand of the hot strip mill) and from the blooming mill flume flushing into a single scale pit, to which are also added noncontact cooling waters from both mills. During the test only noncontact water was received from the blooming mill, which was not in operation and thus not yielding contact waters. Scale pit effluent flowed to a collection pump where it combined with hot strip mill finishing strand effluent. The combined mill discharge flowed to two settling tanks for solids and oil removal. Overflow passed to 12 deep-bed filters (six for each tank). Filtrate was discharged to receiving waters.

Hot strip mill production was 1,474 MTD (97% of capacity). Wastewater flow was 41.6 m^3/min. Filter loading was 0.31 $m^3/min \times m^2$ vs a design level of 0.55.

TABLE 4-15. HOT FORMING: POLLUTANT REDUCTION, PLANT D

Component	Units	Slabber PSP; Δ	Finish stand PSP; Δ	Rough stand PSP; Δ	SS; FDMMG; Δ	Percent reduction[a]
Flow	m^3/min	24.6	67	10.6	102.2	
pH	S.U.	8.6	7.95	-	8.05	
Ammonia	mg/L	2.5[b]	3.4[b]	2.0[b]	1.8[b]	41
Oil and grease	mg/L	12.6	7.8	8.4	7.0	22.3
Phenol (4AAP)	mg/L	0.07	0.08	0.04	0.07	4.7
Residual chlorine	mg/L	<0.2	<0.2	NA	<0.2	
Total suspended solids	mg/L	117	203	28	23	86
Benzene	μg/L	ND	ND	ND	ND	
Naphthalene	μg/L	ND	ND	ND	ND	
Benzo(a)pyrene	μg/L	ND	ND	ND	ND	
Tetrachloroethylene	μg/L	ND	ND	ND	ND	
Cyanide	mg/L	<0.02	<0.02	<0.02	<0.02	
Total organics	μg/L	ND	ND	2.2	ND	
Lead	μg/L	8.6	25.5	6.6	10.6	45.6
Nickel	μg/L	75[b]	179[b]	83[b]	71[b]	50.7
Zinc	μg/L	<30	<30	30	60[b]	-
Total metals	μg/L	173	265	152	171	
Toxicity, minnow, 96 h	LC_{50}	100% survived in 100%	100% survived in 100%	-	35.4[c]	
Toxicity, daphnia, 48 h	EC_{50}	100% killed in 60%	100% survived in 100%		5.7[d]	

ND = None detected.

[a] Based on composite of slabber, finish train, and rough stand, all combined for treatment.

[b] Exceeds toxicity limits, Table 4-4.

[c] Repeat sample, March 7, 1983 showed >100 percent survival in 100 percent. Original tests were run November 30, 1982.

[d] Repeat sample, March 7, 1983 showed 52.9 percent.

Table 4-16 shows that neither the raw nor treated wastewaters were biotoxic. Concentrations of ammonia, lead, nickel, and zinc slightly exceeded some of the toxic limits, however.

Conclusions

Raw hot-forming wastewaters have shown low biotoxicities, while raw cold rolling waters have shown fairly high biotoxicity. Treatments applied to combined hot forming and cold rolling wastewaters appear to have had little effect on toxicity.

4.6 SLABBING MILLS

Figure 4-6 shows the wastewater treatment systems and sampling points for the two systems studied. Plant A's slabbing mill wastewaters from work roll cooling and scarfing fume control were collected into a primary scale pit and passed to the hot strip mill treatment system (Figure 4-5). Flows during the study were 37.9 m^3/min (normal rate), while production was 6,196 MTD (62% of capacity).

Water from the scale pit, mixed with that from the hot strip mill roughing strands, scale pit waters from the runout tables and coilers of the hot-strip mill, and pretreated combined waters from the hot strip mill finishing strand and cold rolling mill (Δ^a in Table 4-17), flows to the central treatment plant previously described. Samples were taken at the primary scale pit and the roughing strand scale pit.

Test results, Table 4-17, indicated that the raw wastewaters from this slab mill were only slightly toxic to minnows, with 100% survival in a 64% dilution. The LC_{50} for daphnia could not be calculated due to an inappropriate choice of dilutions for the test.

Plant B collects slabbing mill roll cooling wastewater and fume control wastewater in a scale pit. These flow along with other waters from the operation to a mixer where polymer is added, then to a treatment basin. There oil is skimmed and the effluent is discharged to receiving waters.

During the study, wastewater flow was 18.9 m^3/min (71% of average). Production was 2,726 MTD (85% of average). Retention time in the basin was 4.5 h vs. 2.5 at maximum design flow.

TABLE 4-16. HOT FORMING: POLLUTANT REDUCTION, PLANT F

Component	Units	Universal mill PSP; Δ	Hot strip finish stand PSP; Δ	SB; SS; Δ	FDSP Δ	Percent reduction
Flow	m^3/min	13.2	28.4	41.6	41.6^{a}	
pH	S.U.	7.35	7.34	7.35	7.26	
Ammonia	mg/L	<0.04	0.6^{b}	-	<0.4	-
Oil and grease	mg/L	19.9	14.0	15.9	8.0	49.7
Phenol (4AAP)	mg/L	<0.06	<0.06	<0.06	<0.06	-
Residual chlorine	mg/L	<0.5	<0.5	<0.5	<0.5	-
Total suspended solids	mg/L	28	41	37	7	81.1
Benzene	µg/L	ND	ND	ND	ND	-
Naphthalene	µg/L	ND	ND	ND	ND	-
Benzo(a)pyrene	µg/L	ND	ND	ND	ND	-
Tetrachloroethylene	µg/L	ND	ND	ND	ND	-
Cyanide	mg/L	<0.02	<0.02	<0.02	<0.02	
Total organics	µg/L	ND	2.3	ND	ND	-
Lead	µg/L	13.7	50.9^{b}	39.1	10.4	73.4
Nickel	µg/L	691^{b}	635^{b}	653^{b}	71.2^{b}	89.1
Zinc	µg/L	28	77^{b}	61.4	44	28.3
Total metals	µg/L	1,419	1,621	1,556	185	88
Toxicity, minnow, 96 h	LC_{50}	Nontoxic	Nontoxic			
Toxicity, daphnia, 48 h	LC_{50}	Nontoxic	Nontoxic			

ND = None detected.

[a] Weighted combined universal mill and hot strip mill wastewaters.

[b] Exceeds toxicity limits, Table 4-4.

	Plant	
	A	B
Primary scale pit	● s	● s
To hot strip mill system	●	
Equalization		●
Flocculation with polymer		●
Surface skimmer		● s
Discharge		●

s = Sample point

Figure 4-6. Hot forming slabbing mills—treatments and sampling.

TABLE 4-17. HOT FORMING, SLAB MILL, HOT STRIP MILL, AND CENTRAL TREATMENT: POLLUTANT REDUCTION, PLANT A

Component	Units	Slab mill	Pretreated hotmill, cold	Hot strip mill		Central treatment				Percent reduction
		PSP →	roll mill →	PSP2[a]; Δ	PSP4; Δ	Δ[b] ST-CL;	CT;	SB; Δ	RC	
Flow	m^3/min	37.9	78	102.2	65.9	284		416		
pH	S.U.	7.9		7.6	7.6			7.7		
Ammonia	mg/L	1.2[c]		<0.4	<0.4	.396		<0.4		Nil
Oil and grease	mg/L	51.5	153	23.7	11.5	60.1		17.8		70
Phenol (4AAP)	mg/L	<0.06		<0.06	<0.06			<0.06		
Residual chlorine	mg/L	<0.2		--	--			0.2		
Total suspended solids	mg/L	94	58.9	76	15	59.6		9		85
Benzene	µg/L	ND		ND	ND			ND		
Naphthalene	µg/L	ND		ND	ND			ND		
Benzo(a)pyrene	µg/L	ND		ND	ND			ND		
Tetrachloroethylene	µg/L	ND		ND	ND			ND		
Cyanide	mg/L	<0.02	<0.02	<0.02	<0.02			<0.02		
Total organics	µg/L	ND		ND	ND			ND		
Lead	µg/L	67[c]	35[c]	8.9	67[c]	37.3[c]		13		65
Nickel	µg/L	178[c]	25.6	24	178[c]	80.7[c]		<19		76
Zinc	µg/L	57[c]	32.3	<28	57[c]	39.8		<28		30
Total metals	µg/L	601	173	118	600	309		123		60
Toxicity, minnow, 96 h	LC$_{50}$	100% survival in 64%						100% survival in 64%		
Toxicity, daphnia, 48 h	EC$_{50}$	Could not calculate						>32		

ND = None detected.

[a] PSP2 collects wastewater from the roughing strands of the plants' hot strip mill.

[b] Total from these sources to control treatment.

[c] Exceeds toxicity limits, Table 4-4.

Samples were taken after the scale pit and after final treatment. Table 4-18 shows no toxicity for minnows in both the raw and treated waters. Lead and nickel were slightly above toxic limits in the raw and treated waters, and zinc exceeded limits in the raw wastewater.

Conclusions

Wastewaters from slabbing mills tested were nontoxic to minnows and from only moderately toxic to nontoxic to daphnia.

4.7 SECTION MILLS

Figure 4-7 shows the treatment systems and sampling points for the section mill wastewaters studied. Plant A recycled 98% of its treated wastewater. Treatment consisted of collection of process waters in a scale pit, with oil skimming; clarification, dilution with noncontact cooling water from various mills, cooling and recycle. Makeup, if needed, was added at the cooling tower. A 2% blowdown was discharged.

Production was 562 MTD during the tests (44% of capacity). Flow was 3.8 m^3/min (50% of design).

Samples were taken after the primary scale pit and after the clarifiers. Test results shown in Table 4-19 indicate no toxicity for minnows for both raw and treated waters. Very slight toxicity for daphnia was reported, in limited fashion, as "could not calculate."

Plant E's section mill wastewater treatment system collects process water in a primary scale pit where oil is skimmed off. The effluent is sent to a cooling tower and thence to recycle. A blowdown from the scale pit goes to central treatment, where collected waters from many plant sources are received, some after preliminary treatment. The central treatment proceeds through equalization, neutralization, flocculation with polymers, and clarification with surface skimming.

Samples were taken at the equalization basin and after the final clarifier. Table 4-20 shows that the section mill raw wastewaters were not toxic to minnows before or after oil skimming. Toxicity to daphnia was very low. The central treatment total influent was very toxic with an LD_{50} of 2.4 for minnows and an LC_{50} of 0.1 for daphnia. Ammonia, residual chlorine, lead, nickel, and zinc all exceeded the toxic limits. Considerable reduction in toxicity occurred

	Plant	
	Bar Mill A	Section Mill E
Primary scale pit	●s	●s
Surface skimmer		●s
Central treatment, equalization		●s
Flocculation with polymer	●	
Flocculation with aluminum	●	
Flocculation with lime	●	
Acidification	●	
Clarifier	●s	●s
Cooling tower	●	
Recycle	●	
Discharge		●

s = Sample point

Figure 4-7. Hot forming section mills—treatment and sampling.

TABLE 4-18. HOT FORMING SLAB MILL: PRIMARY POLLUTANT REDUCTION, PLANT B

Component	Units	PSP Δ	E	FLP	SS Δ	Percent reduction
Flow	m^3/min	18.9			18.9	
pH	S.U.	6.0			6.0	
Ammonia	mg/L	<0.4			<0.4	-
Oil and grease	mg/L	134			73.4	48.2
Phenol (4AAP)	mg/L	<0.02			<0.02	-
Residual chlorine	mg/L	<0.2			<0.2	-
Total suspended solids	mg/L	250			22	91.2
Benzene	µg/L	ND			ND	
Naphthalene	µg/L	ND			ND	
Benzo(a)pyrene	µg/L	ND			ND	
Tetrachloroethylene	µg/L	ND			ND	
Cyanide	mg/L	<0.02			<0.02	
Total organics	µg/L	ND			ND	
Lead	µg/L	116[a]			37.9[a]	67
Nickel	µg/L	157[a]			101[a]	36
Zinc	µg/L	131[a]			<10	92
Total metals	µg/L	792			198.6	75
Toxicity, minnow, 96 h	LC_{50}	100% survival in 100% effluent			100% survival in 100% effluent	
Toxicity, daphnia, 48 h	EC_{50}	100% survival in 100% effluent			100% survival in 100% effluent	

ND = None detected.

[a] Exceeds toxicity limits, Table 4-4.

TABLE 4-19. HOT-FORMING BAR MILL: POLLUTANT REDUCTION, PLANT A

Component	Units	PSP; Δ	FLP;	FLA;	FLL;	A;	CL; Δ	† CT;	RC	Percent reduction
Flow	m³/min	3.8					3.8			
pH	S.U.	8.1					8.0			
Ammonia	mg/L	<0.4					<0.4			
Oil and grease	mg/L	57					17.2			70
Phenol (4AAP)	mg/L	<0.02					0.03			
Residual chlorine	mg/L	0.2					<0.2			
Total suspended solids	mg/L	110					24			78
Benzene	µg/L	ND					ND			
Naphthalene	µg/L	ND					ND			
Benzo(a)pyrene	µg/L	ND					ND			
Tetrachloroethylene	µg/L	ND					ND			
Cyanide	mg/L	<0.02					<0.02			
Total organics	µg/L	ND					ND			
Lead	µg/L	112[a]					20			82
Nickel	µg/L	74[a]					15			80
Zinc	µg/L	<28					<28			
Total metals	µg/L	284					97			66
Toxicity, minnow (96 h)	LC_{50}	100% survival in 100%					100% survival in 100%			
Toxicity, daphnia (48 h)	EC_{50}	Could not calculate					Could not calculate			

ND = None detected.

[a] Exceeds toxicity limits, Table 4-4.

TABLE 4-20. HOT-FORMING, SECTION MILL; POLLUTANT REDUCTION, PLANT E

Component	Units	PSP; Δ	SS ; RC; CNT Δ	Central treatment CPT;CYPT; E; ↑Δ	Central treatment NC;NA;FLP;CL;SS Δ	Percent reduction
Flow	m^3/min	7.6	7.6	2.6	2.6	
pH	S.U.	7.9	7.8	10.9	7.51	
Ammonia	mg/L	1.8^b	$<0.4\ (78)^a$	4.6^b	5.8^b	-
Oil and grease	mg/L	16.6	3.2 (88)	34.1	<1	97
Phenol (4AAP)	mg/L	0.03	<0.02 (33)	0.11	0.07	36
Residual chlorine	mg/L	$<0.2^b$	$<0.2^b$	$<0.2^b$	$<0.2^b$	
Total suspended solids	mg/L	101	61 (40)	1,046	11	98
Benzene	µg/L	ND	ND	ND	ND	
Naphthalene	µg/L	ND	ND	76.3	ND	
Benzo(a)pyrene	µg/L	ND	ND	ND	ND	
Tetrachloroethylene	µg/L	ND	ND	ND	ND	
Cyanide	mg/L	<0.02	<0.02	0.04	0.04	
Total organics	µg/L	ND	ND	83.7	11.9	
Lead	µg/L	31^b	24.1 (22)	66.6^b	<1.9	>97
Nickel	µg/L	$9,350^b$	$5,840\ (38)^b$	$62,500^b$	326^b	99.5
Zinc	µg/L	350^b	$270\ (21)^b$	90^b	<20	78
Total metals	µg/L	10,333	6,488 (37)	232,746	492	99.8
Toxicity, minnow, 96 h	LC$_{50}$	Nontoxic	Nontoxic	2.4	65% survival in 100% sample	
Toxicity, daphnia, 48 h	EC$_{50}$	80% survived in 100%	60% survived in 100%	0.1%	38%	

ND = None detected.

[a] Values in parentheses are cumulative reductions.

[b] Exceeds toxicity limits, Table 4-4.

through the system, and the final effluent showed 65% survival for minnows in pure wastewaters, plus an LC_{50} of 38% for daphnia. Ammonia, chlorine, and nickel are suspected sources of this toxicity.

Conclusions

Section mill raw wastewaters tested were not shown to be toxic to minnows. They were slightly toxic to daphnia. Treatments applied included settling, skimming, clarification, and central treatment (along with other wastewaters). No reduction in toxicity was observed for central treatment, of course, under the circumstances.

4.8 PICKLING

Figure 4-8 shows the treatment systems studied and the sampling points for pickling operations. Plant F used a combination of sulfuric, nitric, and hydrofluoric acids in these operations. Acidic rinse waters and fume scrubber waters flow to an agitated equalization tank for treatment with lime to a pH of 8-9. This was followed by: clarification after polymer addition, dilution with noncontact waters, and discharge.

During the study production exceeded rated capacity for the combined acids lines and equaled 15% of capacity for the sulfuric acid line. The overall production was 1,232 MTD. Wastewater flow was 2.3 m^3/min (retention time 8 h in each clarifier).

Samples were taken at the equalization tank and after the clarifier. Table 4-21 shows the raw wastewaters to be very toxic to both minnnows and daphnia. Ammonia, nickel, and zinc concentrations were excessive and pH was low in the raw waters.

Treated waters were nontoxic to minnows, and 75% of the daphnia survived in 100% sample. Metals content was reduced 99.7%. Ammonia was somewhat high as was nickel.

Plant B used only hydrochloric acid in pickling operations. Collected wastewaters from rinses, fume scrubbing, and miscellaneous process usage were pumped to the cold rolling wastewater treatment system. Flows during the study were 3.8 m^3/min (67% of normal). Production averaged 1,361 MT per turn.

The cold rolling treatment system received waters from temper mills, slitters, grinders, and the pickling units. The combined waters were subjected

	Plant	
	Combination F	HCl B
Surface skimmer		Pickling wastewater s Cold rolling wastewater s ●s(waters combined)
Equalization	●s	●
Air oxidation		●
Neutralization with lime	●	●
Flocculation with polymer		●
Clarifier	●s	●s
Thickener		●
Discharge	●	●

s = Sample point

Figure 4-8. Pickling—treatments and sampling.

TABLE 4-21. PICKLING: POLLUTANT REDUCTION, PLANT F, COMBINATION

Component	Units	E; Δ	NL; CL Δ	Percent reduction
Flow	m^3/min	2.3	2.3	
pH	S.U.	2.45	7.45	
Ammonia	mg/L	1.9^a	1.9^a	
Oil and grease	mg/L	1.5	2.4	
Phenol (4AAP)	mg/L	<0.06	<0.06	
Residual chlorine	mg/L	<0.5	<0.5	
Total suspended solids	mg/L	169	6	96.4
Benzene	µg/L	ND	ND	
Naphthalene	µg/L	ND	ND	
Benzo(a)pyrene	µg/L	ND	ND	
Tetrachloroethylene	µg/L	ND	ND	
Cyanide	mg/L	0.02	<0.02	
Total organics	µg/L	2.8	ND	
Lead	µg/L	8.2	2.4	71
Nickel	µg/L	$14,900^a$	65.2^a	99.6
Zinc	µg/L	72^a	17	76.4
Total metals	µg/L	56,881	190	99.7
Toxicity, minnow, 96 h	LC_{50}	6.9	Nontoxic	
Toxicity, daphnia, 48 h	EC_{50}	4.3	75% survived in 100% sample	

ND = None detected.

[a] Exceeds toxicity limits, Table 4-4.

to oil skimming, air oxidation of ferrous ions to ferric ions, neutralization with lime, clarification after polymer addition, and discharge to receiving waters. Samples were taken of the raw pickling wastewater, the cold rolling mill discharge after the surface skimmer, and combined streams after clarification. Production was above average at 1,430 MTD. Wastewater flow was 1.9 m^3/min (83% of average). Holding time in the clarifiers was 48 min.

Table 4-22 shows low toxicity for the raw cold rolling wastewaters and the final treated waters. Eighty to 100 percent of the minnows survived. All the daphnia were killed in 95% waste, probably due to additives that were not determined in the analysis, although nickel was excessively high and and pH was low in the raw waters, as was ammonia.

Conclusions

Raw wastewaters from pickling showed high biotoxicity to both test organisms. Treatment with lime and clarification reduced the toxicity substantially in one system. Blending the cold rolling wastewaters and flocculation by internally generated ferric ions, addition of lime, and clarification practically eliminated the toxicity of the combined wastes to minnows.

4.9 COLD FORMING

Figure 4-9 shows the treatment systems and sampling points for the cold forming wastewaters studied. Plant A's recycle system has already been described. Pretreatment of the wastewater prior to passage to the hot forming treatment system of this plant included a primary scale pit with oil skimming.

Plant A's once-through system is separate. Collected waters from roll cooling and lubrication with animal tallow are sent to an oil separation basin. Oil is skimmed, and the waters flow to a central treatment system and discharge.

Samples were taken at the inlet and outlet of the oil separation basin. Performance of the central treatments was not assessed.

Production was 753 MTD (60% of capacity). Total water flow was estimated at 0.56 m^3/min (75% of normal).

Table 4-23 shows the raw waters to be nontoxic to minnows. The toxicity to daphnia was indeterminate on the raw waters and high at 4.2 on the skimmed sample. Suspected causes are the high oil and grease and other organics.

TABLE 4-22. PICKLING AND COLD ROLLING: POLLUTANT REDUCTION, PLANT B, HCl

Component	Units	Pickling rinse and scrubber Δ	Cold rolling discharge Δ	SS; FLF; A; AO; NL; FLP; CL Δ	Δ	Percent reduction
Flow	m^3/min	3.8	1.9	5.3	5.3	
pH	S.U.	1	6.5	-	5.0	
Ammonia	mg/L	2.5[a]	-	-	-	
Oil and grease	mg/L	27.7	885	-	4.3	98.6
Phenol (4AAP)	mg/L	0.04	-	-	-	-
Residual chlorine	mg/L	<0.2[a]	-	-	-	-
Total suspended solids	mg/L	7	55	-	9	60
Benzene	µg/L	ND	ND	ND	ND	
Naphthalene	µg/L	ND	ND	ND	ND	
Benzo(a)pyrene	µg/L	-	ND	ND	ND	
Tetrachloroethylene	µg/L	ND	ND	ND	ND	
Cyanide	mg/L	<0.02	-	-	-	
Total organics	µg/L	ND	2.2	3.2	3.9	
Lead	µg/L	15.1	7.6	17.2	<1.9	85
Nickel	µg/L	375[a]	98.2[a]	199[a]	12.3	96
Zinc	µg/L	126[a]	46	91[a]	<10	90
Total metals	µg/L	1,900	365	835	84	90
Toxicity, minnow, 96 h	LC_{50}	8.84	80% survival in 100% waste		100% survived in 100% waste	
Toxicity, daphnia, 48 h	EC_{50}	90% killed in 6.25%	100% killed in 95% waste		100% killed in 95% waste	

ND = None detected.

[a] Exceeds toxicity limits, Table 4-4.

	Plant		
	Recycle A	Once Through A	Once Through B
Primary scale pit	● s		● Raw wastewater
Settling basin		● s	
Surface skimmer	●	● s	● s Pickling wastewater added
To hot forming hot strip mill system at floculation with polymer	●		
Central treatment		●	
Flocculation with lime chloride			●
Air oxidation			●
Neutralization with lime			●
Flocculation with polymer			●
Clarifier	● s		● s
Central treatment settling basin	● s		
Discharge		●	●

s = Sample point

Figure 4-9. Cold forming--treatments and sampling.

TABLE 4-23. COLD FORMING, ONCE-THROUGH TANDEM MILL: POLLUTANT REDUCTION, PLANT A

Component	Units	SB; Δ	SS; Δ	CNT[a]	Percent reduction
Flow	m^3/min	0.6	0.6		
pH	S.U.	8.0	7.7		
Ammonia	mg/L	-	-		
Oil and grease	mg/L	566	217		62
Phenol (4AAP)	mg/L				
Residual chlorine	mg/L				
Total suspended solids	mg/L				
Benzene	µg/L	ND	ND		
Naphthalene	µg/L	30	32.4		-
Benzo(a)pyrene	µg/L	ND	ND		
Tetrachloroethylene	µg/L	3.6	5.1		-
Cyanide	mg/L	-	-		-
Total organics	µg/L	80.1	88.9		-
Lead	µg/L	42[b]	10		76
Nickel	µg/L	37.3	11		71
Zinc	µg/L	<28	<28		-
Total metals	µg/L	206	87		58
Toxicity, minnow, 96 h	LC_{50}	100% survival in 100% waste	100% survival in 100% waste		
Toxicity, daphnia, 48 h	EC_{50}	could not be calculated	4.2		

ND = None detected.

[a] Not the central treatment system sampled, see Table 4-18.

[b] Exceeds toxic limits, Table 4-4.

Plant B's cold rolling wastewater treatment was discussed in Section 4.8, Pickling.

4.10 HOT COATING

Figure 4-10 shows the treatment system and sampling points for the hot coating wastewaters studied. Waters from rinsing acid, alkali, and electrolytic cleaner were collected along with fume hood scrubber waters, and sent to equalization, where spent pickling solution was added. Overflow passed to a blending tank where recycled underflow from the clarifier and effluent from the vacuum filter were added. The mixed waters passed to neutralization where lime and polymer were added, then to a clarifier (holding time 3 h). The overflow was discharged. At equalization, the pH was held at 4.5 by lime addition.

During the study, flow was 4.9 m^3/min (80% of normal). Production averaged 1,172 MTD (69% of average).

Samples were taken after equalization and after clarification.

Table 4-24 shows that the raw waters were highly toxic to minnows and to daphnia. The treated waters were nontoxic, although the ammonia and zinc concentrations exceeded toxicity limits.

Conclusions

The flocculation with lime and clarification effectively reduced wastewater toxicity of hot coating wastewaters studied. There were no organics present.

4.11 CENTRAL TREATMENT

The systems studied have been described in Section 4.5, Hot Strip and Cold Rolling Mills, and Section 4.7, Section Mills. The processes employed are summarized in Figure 4-11.

	Plant C
Equalization	● s
Neutralization with lime	●
Flocculation with polymer	●
Clarifier	● s
Discharge	●

s = Sample point

Figure 4-10. Hot coating galvanizing—treatments and sampling.

TABLE 4-24. HOT COATING, GALVANIZING: POLLUTANT REDUCTION, PLANT C

Component	Units	E; Δ	NL;	FLP;	VF CL Δ	Percent reduction
Flow	m³/min	4.9			4.9	
pH	S.U.	2.8^a			7.5	
Ammonia	mg/L	21.9^a			18.5^a	15.5
Oil and grease	mg/L	1.4			1.4	
Phenol (4APP)	mg/L	<0.02			<0.02	
Residual chlorine	mg/L	<0.2			<0.2	
Total suspended solids	mg/L	115			2	98.3
Benzene	µg/L	ND			ND	
Naphthalene	µg/L	ND			ND	
Benzo(a)pyrene	µg/L	ND			ND	
Tetrachloroethylene	µg/L	ND			ND	
Cyanide	mg/L	0.07			0.03	57.1
Total organics	µg/L	ND			ND	
Lead	µg/L	149^a			<2	98
Nickel	µg/L	65^a			10	85
Zinc	µg/L	$99,000^a$			$2,330^a$	97.6
Total metals	µg/L	100,816			2,422	
Toxicity, minnow, 96 h	LC_{50}	3.9			100% survival in 100% waste	
Toxicity, daphnia, 48 h	EC_{50}	4.1			100% survival in 100% waste	

ND = None detected.

[a] Exceeds toxicity limits, Table 4-4.

	Plant	
	A	E
Scalp tank with chlorination	● s	
Cooling tower	●	
Settling basin	● s	
Recycle	●	
Chrome pretreatment		● s
Cyanide pretreatment		●
Equalization		● s
Neutralization with caustic		●
Neutralization with acid		●
Flocculation with polymer		●
Clarifier		●
Surface skimmer		● s
Discharge	●	

s = Sample point

Figure 4-11. Central treatment—systems and sampling.

5.0 QUALITY ASSURANCE

5.1 QUALITY ASSURANCE PROJECT PLAN

The approved QA Project Plan prepared by PedCo Environmental for sampling and analysis of iron and steel industry wastewaters under Contract No. 68-02-3173 was, by mutual agreement, also used by RTI also in the collection, analysis, and reporting of data.

5.2 OBJECTIVES AND STANDARDS

Quality assurance (QA) objectives were established for measurement data in terms of precision, accuracy, completeness, representativeness, and comparability [14]. Accuracy was determined by analysis of Standard Reference Samples (SRS), by spike samples and blanks, and by assessment of specific steps in the methods of analysis. Precision was determined on the basis of replicate results and comparative results on 10 percent of the samples which were exchanged between both laboratories. Completeness was assessed in terms of the percentage of the total proposed samples which were analyzed and met the precision and accuracy requirements of the program.

Systems audits were conducted to insure compliance with the sampling and analysis requirements set forth in the QA plan and any applicable reference procedures contained therein. Personnel who collected and analyzed the samples were interviewed prior to sampling and before initiation of the analyses. In addition, the analysts were spot-checked on a random basis during the course of their work. The proposed sample collection and analysis procedures were reviewed, and the sampling equipment was inspected and found to be acceptable prior to undertaking the field work. Particular attention was given to the dissolved oxygen meter, and replacement of the membrane therein was required. Thereafter, the meter performed acceptably.

Sample custody forms and labels were reviewed and found to be acceptable, the proposed packaging and icing of samples in sample storage arrangements were found to be acceptable. Sample collection, preservation, and field analysis procedures were also reviewed and found to be acceptable. Procedures for collection of volatile organic samples were evaluated by requiring one of the field personnel to collect dummy VOA samples from a laboratory tap. The procedure was observed to be acceptable.

Audits of chemical analyses at RTI were conducted for phenol, ammonia, oil and grease, and metals. Corrective actions were implemented when control limits on precision or accuracy were exceeded. Whenever unacceptable QA sample results were reported, reviews of the entire procedure and data reduction process were conducted. For example, the initially reported results for the ammonia performance evaluation sample were unacceptable. Discussions with the analyst disclosed an error in the reading of concentrations obtained from a graph of the ammonia electrode response versus concentration. A rereading of the graph and subsequent recalculation resulted in a value within the acceptable range.

Prior to preparation of the final report, data were reviewed for reasonableness with respect to the stream sampled, the procedures used, and the results obtained. Calculation and reporting errors identified at this time were corrected and, where necessary, laboratory notebooks were reviewed for confirmation of data quality. Audits of analyses for organics by Mead CompuChem were conducted by that firm. These are described in the Precision Section.

Bioassays were audited by examination of the notebook records and personal interviews with the EPA laboratories at Athens and Wheeling.

Performance audits of analyses were based on the results of testing of Standard Reference Solutions (SRS) from PedCo Environmental, and from EPA at Cincinnati. The SRS's were, to the extent possible, samples prepared and used by PedCo for previous and current analyses of iron and steel industry wastewaters. PedCo samples were used for total suspended solids, fluorides, chromium, lead, iron, cadmium, copper, arsenic, nickel, selenium, zinc, and antimony. Ammonia data quality was evaluated using two EMSL-C Nutrient Quality Control Samples. Oil and grease test results audits were evaluated by analyses of an aliquot of sunflower oil taken through the analyses procedure. Phenol and cyanide performances were assessed based on recoveries obtained in the distillation step of the prescribed methods.

5.3 PRECISION

Precision was defined, except for GC/MS methods, by the coefficient of variation (CV) of analytical test results:

$$CV = \frac{S}{\overline{X}} = \frac{\left[\frac{(X_1 - X_2)^2}{2}\right]^{\frac{1}{2}}}{\frac{X_1 + X_2}{2}}$$

where X_1 and X_2 = values of the replicate test results,

S = the estimated standard deviation of the replicates, and

$\overline{X}$ = the mean of the replicates.

The value of the CV must have been within the 99.5 percentile (upper control limit = 2.28 x CV), or the analysis was voided and the entire batch of samples reanalyzed. Values of the upper control limit, developed from replicate analysis of wastewater samples and standard reference solutions (SRS's) are given in Table 5-1 together with the CV's obtained at RTI during metals analyses.

5.4 ACCURACY

The accuracy of the analyses was assessed, based on whether the results obtained for the performance evaluation samples were within the 2σ control limits set forth in the PedCo QA Plan. The results are summarized in Table 5-2. Results for all metals, fluoride, total suspended solids, and ammonia were within the acceptable 2σ limits, except for Sb which was slightly lower than the acceptable limit. The impact of this on the test results for the wastewater stream is unclear since all of the reported Sb results were considerably lower than the SRS concentration and near the detection limit by electrothermal atomization atomic absorption.

Results for oil and grease were 5 percent higher than expected for a large spike of 1.59 g. Spikes of 15 and 19 mg were used and also gave results 5 percent higher than expected.

TABLE 5-1. SPECIFICATIONS FOR ANALYTICAL RESULTS

Constituent	Upper control limit, 2.8 CV, fraction	CV obtained during study[a], fraction	RTI detection limits, µg/L
Antimony	0.196	0.003 - 0.235[b]	5
Arsenic	0.389	0.009 - 0.18	3
Copper	0.129	0.005 - 0.076	1
Cadmium	0.216	0.101 - 0.67[b]	0.1
Selenium	0.154	0.004 - 0.136	10
Zinc	0.064	-	1
Chromium	0.123	0.003 - 0.046	2
Lead	0.095	0.019 - 0.20[b]	3
Iron	0.050	-	10
Nickel	0.109	0.025 - 0.134[b]	5
Total cyanide	0.269	-	4
Ammonia	0.059	-	20
Fluoride	0.232	-	50
Oil and grease	c	c	1000
pH	0.036[d]	-	-
Phenolics (4AAP)	0.078	0.013 - 1.2[b]	30
Residual chlorine	c	-	-
Total suspended solids	0.202	-	

[a] Replicate analyses of prepared sample.

[b] Set of analyses was rerun when CV exceeded the indicated upper limit.

[c] Insufficient data to establish a value.

[d] Single laboratory precision taken from Methods for Chemical Analysis of Water and Wastes EPA 600/4-79-020.

TABLE 5-2. ANALYSES OF PedCo, EPA AND IN-HOUSE QA SAMPLES AT RTI
(μg/L unless otherwise noted)

Analyte	Expected concentration	2σ control limits	Reported concentration
Sb	150	120-180	113
Cd	7.5	6.3-8.7	7.31
Cr	50	44.4-55.6	47.7
As	75	65.6-84.6	81.9
Cu	75	67.4-82.6	78.9
Fe	6000	5800-6200	6100
Pb	150	129-171	147
Ni	150	130-180	159
Se	50	46-54	54.7
Zn	1500	1370-1630	1551
Phenolics[a]	-	-	-
F	1600	1340-1860	1610
TSS	135,000	134,600-145,400	141,000
CN[b]	-	-	-
Oil and grease	1.59 g	-	1.51 g
Ammonia	150	-	155
	1500	-	1530

---

[a] 104 percent recovery obtained.

[b] 92-95 percent recovery obtained.

Results for ammonia were well within the EMSL-C acceptance limits for these samples.

A phenol standard was analyzed at RTI with and without the distillation step of the prescribed method (4-AAP). This was done to evaluate the effect of the sample distillation on phenol recovery. A recovery of 104 percent was obtained and was accepted under the limits set by PedCo (±10 percent). Subsequent standards were shown to have the same photometer response.

Cyanide recovery was evaluated by analysis of two distilled water samples spiked with cyanide at 50 and 100 µg/L, respectively. These spiked samples were then carried through the distillation procedure. Recoveries of 92 and 95 percent were obtained. These are considered acceptable.

5.5 PRECISION AND ACCURACY METHODS 624 AND 625

Aliquots of collected samples were analyzed for priority pollutants by RTI's subcontractor, Mead CompuChem, or by PedCo if that firm did the sampling. Detection limits ranged above the minimum (usually ~ 10 µg/L) for some samples and pollutant categories because the samples were diluted to avoid saturation of the mass spectrometer's detection system by other compounds present at high concentrations, or because the responses were obtained at lowered sensitivity.

Complete analytical reports, including chromatograms, mass spectra, calibration, and quality-control data, are available for the data from each plant involved.

At this time, good estimates of the accuracy and precision of Methods 624 and 625 are not available (Quality Assurance Plan, June 1982, and CFR 40-136). Results by these GC/MS methods are judged by the absence of interference and contamination and by the percent recovery and standard deviation of surrogate spikes and matrix spikes, and by replicate analyses.

The quality control measures employed during this study included: instrument tuning and calibration three times daily; reagent blanks; surrogate spikes in all samples, matrix spikes, method blanks at least every 20 samples, and duplicate analyses.

When volatile organics were analyzed, DFTPP could not be used because of its low volatility. Bromofluorobenzene (BFB) was used instead. Tables 5-3 and 5-4 show specified ion abundancies for these standard compounds.

TABLE 5-3. DECAFLUOROTRIPHENYLPHOSPHINE, KEY IONS AND ION ABUNDANCE

Mass	DFTPP specs
51	30 to 60 percent of mass 198
68	Less than 2 percent of mass 69
70	Less than 2 percent of mass 69
127	40 to 60 percent of mass 198
197	Less than 1 percent of mass 198
198	Base peak 100 percent relative abundance
199	5 to 9 percent of mass 198
275	10 to 30 percent of mass 198
365	Greater than 1 percent of mass 198
441	Present but less than mass 443
442	Greater than 40 percent or mass 198
443	17 to 23 percent of mass 442

TABLE 5-4. BROMOFLUOROBENZENE, KEY IONS, AND ION ABUNDANCE

Mass	BFB specs
50	20 to 40 percent of mass 95.
75	50 to 70 percent of mass 95.
95	Base peak, 100 percent relative abundance.
96	5 to 9 percent of mass 95.
173	Less than 1 percent of mass 95.
174	70 to 90 percent of mass 95.
175	5 to 9 percent of mass 95.
176	70 to 90 percent of mass 95.
177	5 to 9 percent of mass 95.

5.6 TUNING THE GC/MS

Once per 8-hour shift, the instrument was fine-tuned using decafluorotriphenylphosphine (DFTPP) or bromofluorobenzene (BFB). The mass spectrum obtained for DFTPP met the criteria described by Harris et al. [20]; or adjustments were made until a match was obtained.

5.7 CALIBRATION

After the instrument met the key ion and ion abundance criteria for the above-mentioned compounds, it was calibrated. Calibration curves were generated from the results of analyses of at least three solutions of known concentrations of pure chemicals or standards. These standard concentrations were evenly distributed throughout the range of the method corresponding to nominally 10, 40, and 200 µg/L.

D_{10}-anthracene (the internal standard) was also injected at a constant amount, nominally 100 ng. From these data, external and internal standard libraries were generated. For the internal calibration method, response factors versus concentrations versus the integrated heights were plotted. After the master set of instrument calibration curves had been established, they were verified daily by injecting at least one standard solution. If significant drift had occurred, a new calibration curve was constructed.

For volatile organic analysis, 100 ng each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane were used as internal standards. A calibration curve was prepared. The response factor (RF) was plotted against the standard concentration using a minimum of three concentrations over the range of interest. Once this calibration curve had been determined, it was verified daily by introducing at least one standard solution containing the appropriate internal standard with each sample. If significant drift were observed, a new calibration curve was constructed.

The response factor, RF, is the ratio of the calibration factors for the standard solution and the internal standard:

$$\text{RF} = \frac{\dfrac{\text{area of the characteristic ion of the standard used}}{\text{concentration of the standard}}}{\dfrac{\text{area of the characteristic ion of the internal standard}}{\text{concentration of the internal standard}}}$$

After calibration was completed, sample analysis began. A typical run log sequence was as follows:

Standard
Blank Organic-free water
Sample 1
2
3
4
5
6
Blank Organic-free water
Sample 7
8
9
10
11
12
Standard
Blank
Sample 13

This cycle was continued until the run was completed. However, if there was a shift overlap in running these samples, a new DFTPP sample was inserted at the beginning of each 8-hour shift.

Duplicates and spikes were processed approximately one in every 20 samples to further monitor the performance of the GC/MS. In addition, surrogate standards were used with each sample processed.

Blind samples were routinely sent to the laboratory for analysis. These consisted of replicates as well as external quality control samples. These samples were obtained from outside sources and contained known concentrations of specific compounds. They were submitted to the laboratory on a regular basis. This was done at least once a month for every shift.

5.8 REAGENT BLANKS

With each new lot of reagents, a reagent blank was prepared and analyzed to assure that the reagents did not introduce contaminants or interferences.

5.9 SURROGATE SPIKES AND EXTRACTION CONTROLS

Each extraction batch had at least one quality assurance sample included (blank, spike, or replicate). Method blanks were generated by passing a clean matrix through the entire analytical scheme. At least one method blank was run for every 20 samples and whenever reagent lots changed. Replicates were utilized to determine the precision of the procedure under real operating circumstances.

Before each sample was extracted, a minimum of two surrogate standards were added at concentrations of 100 µg/L. These surrogate standards were quantitatively analyzed in the GC/MS phase. Historical records were maintained on the percent recovery of the surrogate standards for each sample. These data form the statistical basis upon which the extraction technique is monitored.

The controls specified for surrogates, duplicates, blanks and matrix samples are shown below. Any sample for which surrogate recoveries fell outside two standard deviations (which is tighter than the recommended three) were reviewed by the Quality Control Board. This Board, which consists of the Vice President-Operations, the Chief Chemist, and the Quality Control Officer, reviewed all relevant quality control information for any sample outside control and made recommendations to the President. If there were any uncertainty as to the validity of the data, the sample was re-analyzed and this additional information reviewed by the Board.

SURROGATE SPIKE CONTROLS

	Recovery	Duplicates (Relative Percent Difference)
d_6-benzene	80-130	< 35
d_8-toluene	80-140	< 20
d_5-nitrobenzene	20-85	< 60
2-fluorophenol	35-110	< 60
d_8-naphthalene	30-105	< 45
2-fluorophenol	15-80	< 55
d_6-phenol	10-50	< 60

MATRIX AND BLANK SPIKE CONTROLS

	Matrix	Blank
heptachlor	65-125	80-120
aldrin	70-115	80-115
dieldrin	80-110	80-115
1,4-dichlorobenzene	20-105	0-110
1,2,4-trichlorobenzene	20-100	25-100
2,4-dinitrotoluene	20-70	20-70
pyrene	65-130	65-140
acenaphthene	45-95	50-100
2-chlorophenol	40-90	30-100

MATRIX AND BLANK SPIKE CONTROLS (con.)

	Matrix	Blank
phenol	10-40	15-40
p-chloro-m-cresol	30-90	35-95
pentachlorophenol	45-135	45-140
benzene	70-125	90-130
chlorobenzene	90-135	95-135
toluene	85-130	90-125

(N-nitrosodi-n-propylamine and 4-nitrophenol are also monitored, but due to well-known capricious nature of these compounds it has not yet been possible to establish meaningful controls).

5.10 METALS

Samples were analyzed for metals using flame and furnace atomic absorption spectrophotometry. The analysis procedure involved two steps: sample digestion with nitric acid and subsequent instrumental analysis.

For each batch of samples in the digestion process, a method blank was included. This blank was analyzed along with the samples to assure that no contaminants were introduced by the reagents or laboratory procedures.

For each element analyzed, a five-point calibration curve was prepared using standard solutions covering the concentration range of interest. System blanks, method blanks, and a standard solution were also run every 10 samples during the analysis sequence. The accuracy and precision of these measurements fell within the guidelines found in "Methods for Chemical Analysis of Water and Wastes (EPA-600/4-79-020)" if available for the element in question. If that guideline was absent, the manufacturer's literature was used to establish limits.

5.11 BIOASSAY QUALITY ASSURANCE, ACCURACY, AND PRECISION

Bioassays were conducted by exposing organisms (fathead minnows and daphnia) to several different concentrations of the samples in dilution water and observing the number of survivals daily for up to 4 days (fathead minnows) or up to 2 days (daphnia). The test protocols were essentially those prescribed by Peltier and Weber [15]. Replicate tests were run using 10 organisms for each test.

Test organisms at Athens were exposed to a standard toxic substance, sodium pentachlorophenate, using the test protocol. The results for April and May were as follows:

Date	5-9 day-old fathead minnows		24-hour-old Daphnia pulex	
4/14-15/83	LC_{50}	0.16 mg/L	LC_{50}	1.5 mg/L
5/12-3/83	LC_{50}	0.215 mg/L	LC_{50}	1.5 mg/L

The Wheeling Laboratory maintained "Precision Control Charts" on normalized toxicity tests, that is, one of the test results was assigned the value "100" and the other was ratioed: $(X_2/X_1) \times 100$. An UCL was established for this normalized range at 39.6 percent. The results reported were within the laboratory's control range.

During the tests of wastewater samples, controls were run using only dilution water. If more than 20 percent of the organisms died in the controls, the tests were considered invalid. The mortalities for Athens and Wheeling were well below this limit.

For each toxicity test, the LC_{50} and, if possible, the 95-percent confidence interval are calculated on the basis of the volume percent of the effluent in the test solutions. The "volume percent" equals (100 × volume of effluent)/(volume of effluent + volume of dilution water). A wide variety of methods are available to calculate a LC_{50} and EC_{50}, including the log-concentration-versus-percent-survival, probit, and Litchfield-Wilcoxon methods. Use of the Litchfield-Wilcoxon and probit methods require partial mortalities at dilutions above and below the LC_{50}. Most of the samples of this study did not yield this kind of data, there being a rapid fall in survival to 0 after a few partial mortalities. As is frequent in effluent toxicity tests, there were for some samples no partial mortalities at any effluent concentration. In these cases, survival fell from 100 percent at one or more lower effluent concentrations to 0 at the next highest concentration. When this occurs, it is not possible to calculate a confidence interval, and the log-concentration-versus-percent-survival method must be used. The log-concentration-versus-percent-survival method was adopted for use with data for this study.

While accuracy was controlled by checks on the culture of the organisms, by a toxicity control sample, and by blanks, precision was not calculable via the Litchfield-Wilcoxon procedure for 95-percent confidence limits because of the lack of sufficient partial mortalities above and below the 50-percent survival level.

RTI has therefore assessed the test precision by the coefficient of variation of the two estimates of LC_{50} obtainable by the log-concentration plots. These are given in Table 5-5. In a few cases, where both replicates were needed to identify an LC_{50} value, no estimate of CV was obtainable.

5.12 COMPARABILITY

Several samples were analyzed both at PedCo and at RTI during the study. These "split samples" provide a comparison between the two laboratories. The results are given in Table 5-6.

5.13 COMPLETENESS

All samples were carried through the analyses as planned, except for one sample submitted to EPA-Newtown for bioassay which was accidently lost when the container broke, three unacceptable metals analyses, and one split sample that was delayed too long in shipment to qualify for analysis. The completeness was well over the 90-percent goal set for the study.

TABLE 5-5. BIOASSAY TEST PRECISION

		LC_{50} and coefficient of variation, %			
		Minnow		Daphnia	
Sample	Laboratory	LC_{50}	CV,%	EC_{50}	CV
Hot oil decanter	Athens	12.2, 12.5	1.7	2.0, 2.3	9.8
Adsorber inlet	Athens	0.6, 0.35	37	1.3, 1.3	0
Adsorber outlet	Athens	1.8, 0.37	93	1.3, 1.7	19
Dissolved air flotation	Wheeling	18, 33	42	a	
Clarifier outlet	Wheeling	63,80	17	3.5, 7.0	47

[a] EC_{50} determined by use of combined data and did not yield a CV.

TABLE 5-6. COMPARATIVE ANALYTICAL RESULTS

	January 1983		November 1982					
	Raw flushing liquid, Plant B		Equalization tank, Plant C		Section mill, Plant A		QA samples	
Constitutent	RTI (Mead)	PedCo	RTI (Mead)	PedCo	RTI (Mead)	PedCo	RTI (Mead)	PedCo
Antimony (μg/L)	ND	<5	50	180	3.8	ND	88[a]	120-180
Arsenic	77	50	154	320	9	ND	73[a]	66-85
Cadmium	--	--	0.53	ND	0.03	1.1	7.3[a]	6.3-8.7
Copper	12	19.5	354	244	52.2	43.6	73.1[a]	67-83
Lead	--	--	76.7	--	93.5	112	110[a]	129-171
Zinc	156	120	1.3	650	0.02	<28	180[a]	137-163
Chromium	--	--	163	--	34.6	25.2	45.9[a]	44-56
Selenium	2,790	1,020	1,850	1,300	ND	ND	43.4[a]	46-54
Nickel	--	--	36.2	--	67.8	74	149.5[a]	130-180
Cyanide	<20	<20	--	<0.02	1.0	<0.02	--	--
Phenol (4-AAP) (mg/L)	919	589	812	831	958	<0.02	19,230	18,490
Fluorides	--	--	65	--	0.2	0.21	1.6	1.6
Ammonia	3,970	3,291	665	1,010	3.9	<0.4	54	60
Residual chlorine	--	--	--	--	--	0.2	--	--
Total suspended solids	31	66	--	85/75	30/33	110	135	135
Iron	--	--	10.1	--	18.5	--	5.9	--
Oil and grease	428	80.2	102	26.3	77	57	14.9	(104% recovery)
Acrylonitrile (μg/L)	--	16.6						
Benzene	11,000	8,950	[b]	11,600				
Chloroform	--	ND	--	ND				

See footnotes at end of table.

(continued)

TABLE 5-6 (continued)

Constitutent	January 1983		November 1982					
	Raw flushing liquid, Plant B		Equalization tank, Plant C		Section mill, Plant A		QA samples	
	RTI (Mead)	PedCo	RTI (Mead)	PedCo	RTI (Mead)	PedCo	RTI (Mead)	PedCo
Ethyl benzene	--	20.3	--	9				
Toluene	2,000	5,230	--	1,010				
Xylene	--	1,820	--	825				
Acenaphthene	2,500	ND						
Anthracene	800	ND						
3,4-Benzofluoranthene	700	ND						
Benzo(k)fluoranthene	700	ND						
Phenol	200,000	404,000	--	1,860				
2,4-Dimethylphenol	2,400	ND						
Fluoranthene	1,600	ND	--	12.2				
Fluorene	1,800	ND	--	ND				
2,1,1-Trichloroethyelene	--	--	--	--	53	49.6		
Naphthalene	40,000	56,000	--	783				
Phenanthrene	3,100	ND						
Tetrachloroethylene	--	--	--	--	25	57.4		
1,2-Transdichloroethylene	--	--	--	--	11	ND		
Chrysene	--	775	--	ND				
Acenaphthylene	3,600	6,400	--	ND				
Pyrene	1,000	1,340	--	8.7				

ND = None detected.

[a] NBS SRM 1643a, trace elements in water used as performance evaluation sample.

[b] Priority pollutants not determined because split sample was delayed in shipment.

6.0 SUMMARY OF EFFLUENT TOXICITY DATA

6.1 IRON AND STEEL PROCESS WASTEWATERS

Raw wastewaters from iron and steel manufacturing have been characterized chemically using historical data from a broad range of manufacturers [1]. Pollutant concentrations, based on loadings for model plants, were developed for process subcategories. These are summarized in Table 6-1 for the eight subcategories chosen for biotoxicity evaluation: cokemaking, ironmaking, steelmaking, continuous casting, hot forming, pickling, cold forming, and hot coating. Most of the toxic pollutants are found in cokemaking and cold forming; although, as shown, potentially toxic pollutants are present in all eight wastewaters. All these model processes except cold rolling include some recycling of wastewaters. Water recycle, while reducing overall discharge, would be expected by itself to concentrate wastewaters and increase toxicity.

Control of regulated pollutants, listed in Table 6-2, and other toxic pollutants known to be present, has been assessed for these subcategories, in each of which treatment technologies have been examined as to their demonstration status, application and performance in reducing pollutant concentration. This assessment does not include effectiveness in reducing biotoxicity; hence there is no basis for relating the reductions in toxic chemical content to reductions in biotoxicity. The information gained, however, provides the basis for selection of subcategories for biotoxicity assessment.

The effectiveness of wastewater treatment technologies in reducing biotoxicity is not inherent in outfall compliance data. Nor can these data provide a basis for relating reduction in toxic chemical content to reductions in biotoxicity. Outfalls represent the results of accumulative treatment and collection. These data nevertheless do identify toxicities that persist after currently applied treatments. Therefore, available bioassay test results are summarized in Section 6.2 to identify the current status of treated wastewaters.

TABLE 6-1. IRON AND STEEL MAKING RAW WASTEWATER CHARACTERISTICS[a,b]

Characteristics	Coke making	Iron making	Steelmaking[c]		Contin. Cast.	Hot Forming	Pickling			Cold forming			Hot coating	
			S.C.	W.O.			H_2SO_4	HCl	Comb.	Comb.	Recirc.	Once Thru	Galv.	Terne
Flow, l/kkg	676	13353	4172	4590	14188	14188	864	693[d]	963[d]	1252	104	1669	10013	2503
pH, SU	7-10	6-9	7-12	8-11	6-9	<1-6.4	<1-6.4	<1-5	4-8.2	6-9	6-9	6-9	3-9	2-8
Ammonia-N	600	20												
Oil and grease	75				25	56	11	10	10	1481	14700	1215	25	30
Phenolics (4-AAP)	300	3												
Sulfide	150													
Dissolved iron							2800	1200	740					
Thiocyanate	480													
Residual chlorine														
Total susp. solids	50	1900	720	4200	60	3000	120	30	49	843	1013	135	80	75
Fluorides		15	15	20					1200					
1 Acenaphthene												0.055		
3 Acrylonitrile	1.2													
4 Benzene	3.5[e]													
6 Carbon tetrachloride												0.007		
9 Hexachlorobenzene	0.01													
11 1,1,1-Trichloroethane												0.043		
13 1,1-Dichloroethane														
21 2,4,6-Trichlorophenol	0.1													
22 Parachlorometacresol	0.6													
23 Chloroform	0.3[e]			0.05							0.037			
31 2,4-Dichlorophenol	0.01													
34 2,4 Dimethylphenol	5	0.05												
35 2,4 Dinitrotoluene	0.2													
36 2,6 Dinitrotoluene	0.1													
38 Ethylbenzene	3													
39 Fluoranthene	0.8[e]	0.08								0.071	0.27			
54 Isophorone	0.5													
55 Naphthalene	30[e]									4	1.5	4.4		
60 4,6-Dinitro-o-cresol	0.12										0.063			
64 Pentachlorophenol	0.12													
65 Phenol	275[e]	0.65[e]									0.17			
66-71 Total phthalates	5													

See footnotes at end of table.

(continued)

TABLE 6-1 (continued)

Characteristics		Coke making	Iron making	Steelmaking[c]		Contin. Cast.	Hot Forming	Pickling			Cold forming			Hot coating	
				S.C.	W.O.			H_2SO_4	HCl	Comb.	Comb.	Recirc.	Once Thru	Galv.	Terne
72	Benzo(a)anthracene	0.3										0.16			
73	Benzo(a)pyrene	0.1^e	0.01												
76	Chrysene	0.4^e	0.01									0.11			
77	Acenaphthylene	3.5^e										0.14			
78	Anthracene										0.18	0.14	0.014		
80	Fluorene	0.6^e									0.98	3.5			
81	Phenanthrene										5.1	0.91			
84	Pyrene	0.6^e	0.05^e								0.05	0.3			
85	Tetrachloroethylene										0.02	0.036	0.02		
86	Toluene	25^e										0.012	0.69		
87	Trichloroethylene											0.009			
114	Antimony	0.2^e	0.04						0.54^e	0.38^e		0.031			
115	Arsenic	2^e	0.1^e		0.06^e			0.17^e	0.11^e		0.16^e	0.26^e	0.02	0.25	0.15
117	Beryllium												0.01		
118	Cadmium		0.1^e	0.06	0.4			0.02	0.01	0.01		0.11^e			0.3^e
119	Chromium		0.5	0.6		0.65	1.3	6.9^e	1.0^e	76^e	0.03^e	2.5^e	0.04	2^e	5^e
120	Copper		0.25^e	0.15^e	5.2^e	0.11	5.7	1.3^e	0.72^e	3.8^e	0.89^e	7.1^e	0.17^e	0.08^e	0.6
121	Cyanide	50^e	12^e												
122	Lead		5	8	3.9^e	0.08	6.5	0.2^e	2.6^e	0.05	0.1	2.9^e	0.39	2^e	1.2^e
123	Mercury				0.02										
124	Nickel		0.1^e	0.3^e	0.4		5.7	2.4^e	1.5^e	95^e	0.21^e	3.3^e	0.2^e	0.5^e	1^e
125	Selenium	0.2^e	0.06		0.02	0.08									
126	Silver			0.02	0.08			0.02							
127	Thallium				0.03										
128	Zinc	0.2^e	20^e	6.8^e	14^e	0.7	3.1	5.6	7^e	0.64	0.15^e	3.7^e	0.098	1.0^e	1.5^e
130	Xylene	12^e													
	Tin														3

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[a] From Development Document for Effluent Guidelines and Standards

[b] All concentrations are in mg/L unless otherwise noted.

[c] S.C. = suppressed combustion W.O. = wet open combustion.

[d] Primary carbon with scarfers.

[e] Pollutant found in all samples

TABLE 6-2. REGULATED POLLUTANT LIST, IRON AND STEEL INDUSTRY [1]

4	Benzene
55	Naphthalene
73	Benzo(a)pyrene
85	Tetrachloroethylene
119	Chromium
121	Cyanide
122	Lead
124	Nickel
128	Zinc
	Ammonia
	Oil and Grease
	pH
	Phenol (4AAP)
	Chlorine Residual
	Total Suspended Solids
	Hexavalent Chromium

Persistent toxicity is evident in outfalls from cokemaking and ironmaking, steelmaking, and certain central treatment systems processing combined wastewaters from several processes. Cold-forming effluents tested do not show much toxicity; the treatments need investigation to determine their effectiveness and the loadings involved. No data are available for Hot Coating and Continuous Casting. Three effluents from central treatment showed a range from an LC_{50} of 19.5 percent dilution to no mortality. (LC_{50} is the concentration expressed as volume percent, lethal to 50 percent of the organisms. EC_{50} is the concentration that causes an adverse effect other than mortality to 50 percent of the organisms.)

6.2 SUMMARY OF EXISTING TOXICITY DATA

Existing data generally represent process wastewaters after treatment and/or dilution with noncontact cooling water, and they often are the combined effluents from several processes. The toxicity tests are often accompanied by chemical analyses of the discharged waters. Included are existing data from compliance tests and data submitted with permit applications.

The summaries given in Tables 6-3 to 6-9 are arranged according to process category so that the information may be readily related to that supplied in the guidelines development documents.

6.2.1 Coke-Plant Effluent Toxicity

Much of the existing data on the toxicity of coke-plant wastewaters are for final (treated) effluent, but these data are supplemented by a pilot-plant study and influent/effluent testing at two plants. The data are summarized in Table 6-3 and include various combinations of wastewater streams:

- Process wastewater from cokemaking
- Noncontact water from cokemaking
- Process water diluted with non-contact water
- Wastewater from cokemaking combined with process water from other sources

Chemical analyses of the water are available for most of these toxicity samples. Treatment technologies were taken from the referenced reports when available and supplemented with plant data from Reference 1.

Both the Koppers and Alabama By-Products outfalls were from a single-stage biological treatment of coke-plant wastewaters. Noncontact cooling water is not included in the Koppers effluent. These data show LC_{50} concentrations that range from less than 10 to 56.5 percent, depending on the organism. The fathead minnow appeared to be most sensitive to the Koppers effluent; the bluegill, to the Alabama By-Products effluent.

The third sampled outfall was from the Jim Walters Resources Plant. Wastewater from a chemical plant, a coke plant, and a pipe-lining plant are given biological treatment and then combined with all other wastewaters (blast furnace, mineral wool plant), and sent to a polishing lagoon. The sample was taken from the lagoon.

At the Republic Steel Plant, the coke-plant wastewater, noncontact water, and surface runoff are combined in an aerated lagoon with a retention time of 30 to 35 days. The sample taken from the outfall of the lagoon in 1981 showed no mortality to minnows or waterfleas. However, samples taken in 1978 show a significant mortality to bluegill sunfish in a static 96-hour test.

TABLE 6-3. TOXICITY DATA, COKEMAKING WASTEWATER

No.	Plant	Outfall From[a]	Treatment[b]	Date	Test[c]	Organism[d]	LC_{50} (%)[e]	Reference
1	Koppers Company Woodward, AL	A	ASF,BOA1	8/78	CF-96	LM	32.0	2
				8/81	S-24	PP	<10.0	2,3
				8/81	S-24	DP	14.5	2,3
2	Alabama By-Products Tarrant, AL	A	ASF,BOA1	3/78	S-96	LM	28.5	2,3
				8/81	S-24	PP	44.0	2,3
				8/81	S-24	DP	56.5	2,3
3	Jim Walters Resources Birmingham, AL	A,P,O	BOA1,SL	4/78	CF-96	LM	42.3	2,3
				3/81	S-96	LM	24.0	2,3
				8/81	S-24	PP	15% Mort.	2,3
4	Republic Steel Thomas, AL	A,N,O	ASF,BOA1	2/78	S-96	LM	6.6	2,3
				2/78	S-96	LM	12.9	2,3
				8/81	S-24	PP	NM	2,3
				8/81	S-24	DP	NM	2,3
5	Great Lakes Steel Zug Island, MI	A[f],C,M,N	CL,T,VF,(FLP)	12/78	S-48	DM	NSM	4
				6/81	CF-96	PP	10% Mort.[g]	5
6	Ford Motor Co. River Rouge, MI	A[f],C,M	T,VF,(FLP,CT, FP)	10/79	S-48	DM	NM	6
7	U.S. Steel Clairton, PA	A	Untreated[h]	8/77	S-24	PP	0.06	7
			ASF,DP,BOA1	8/77	S-24	PP	27	7,8
		A[i]		1981	?	PP	Sl. Toxic	9
				1981	?	DM	Mod. Toxic	9
8	EDI/USS Pilot Plant Clairton, PA	A	ASF,DP,BOA1	9/80	CF-96	PP	65% Mort.	10
				10/80	CF-96	PP	15% Mort.	10
			ASF,DP,BOA1, CA	9/80	CF-96	PP	20% Mort.	10
				10/80	CF-96	PP	100% Mort.	10

See footnotes at end of table.

(continued)

TABLE 6-3. (continued)

No.	Plant	Outfall From[a]	Treatment[b]	Date	Test[c]	Organism[d]	LC_{50} (%)[e]	Reference
9	J&L Steel Pittsburgh, PA	A	Untreated[h]	9/77	S-24	PP	0.46	7,11
			Untreated[h]	9/77	S-24	DM	0.65	11
			ASF,DP	9/77	S-24	PP	4.6[j]	7,11
				9/77	S-24	DM	3.3[j]	11
				9/77	S-24	PP	2.8[k]	7,11
				9/77	S-24	DM	3.9[k]	11
10	National Steel Wierton, WV	A	ASF,BOA2	1977	S-24	DM	NM	8
11	Bethlehem Steel Sparrows Point, MD	A	BOA1	1977	S-24	PP	<20	8
12	Shenango Neville Island, PA	A[l]	CLA,CAG	1981	?	?	V. Toxic	9
		A[m]		1981	?	?	V. Toxic	9

[a] Processes are coded as prescribed in Reference 1 (Volume 1, pg.338) with additions:

A: By-product cokemaking
C: Ironmaking
M: Boiler and/or compressor house
N: Noncontact cooling water
O: Surface runoff, drainage
P: Chemical plant and pipe lining

[b] Treatments

ASF: Free-ammonia still
BOA1: Single-stage biological oxidation
BOA2: Two-stage biological oxidation

TABLE 6-3. (continued)

[b]Treatments: (continued)

CA: Carbon adsorption
CL: Clarifier
CLA: Alkaline chlorination
CT: Cooling tower
DP: Dephenolization
FLP: Flocculation with polymer
FP: Pressure filtration
SL: Settling lagoon
T: Thickener
VF: Vacuum filtration

[c]Type of test:

S-n: Static test for n hours
CF-n: Continuous flow test for n hours

[d]Type of test organism:

CV: Cyprinodon variegatus (sheepshead minnow)
DM: Daphnia magna (waterflea)
DP: Daphnia pulex (waterflea)
LM: Leopomis machrochirus (bluegill sunfish)
MB: Mysidopsis bahia (shrimp)
NA: Notropis atherinoides (emerald shiner)
PP: Pimephales promelas (fathead minnow)

[e]LC$_{50}$ = Effluent concentration lethal to 50 percent of the test organisms and is the way most toxicity tests were reported. Other units used to report test results are:

n% Mortality: Percent mortality in 100 percent effluent reported when LC$_{50}$ cannot be calculated
NM: No mortality
NSM: No significant mortality
Mod. Toxic: Moderately toxic
Sl. Toxic: Slightly toxic
V. Toxic: Very toxic

[f]Wastewater from cokemaking is noncontact only.

TABLE 6-3. (continued)

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[g] Low mortality, but fish were lethargic in concentrations $\geq$ 25 percent. Suspect volatile organic compounds.

[h] Untreated influent to wastewater plant was sampled.

[i] Outfall No. 8107271045

[j] Effluent from Treatment Plant 1

[k] Effluent from Treatment Plant 2

[l] Outfall No. 8107271455

[m] Outfall No. 8107281518

The data from Great Lakes Steel include noncontact cooling water from the coke plant. (Process water from the coke plant is discharged to the Detroit wastewater treatment plant.) The sample represents treated wastewater from the blast furnace combined with untreated noncontact water from the blast furnace and coke plant. No significant mortality was observed. The sample taken at Ford Motor Company includes noncontact cooling water and steam condensate from the coke plant which combines with treated effluent from the blast furnaces. The process water from cokemaking is discharged to the sanitary sewer except for final cooler water, which is injected into deep wells.

The U.S. Steel samples from References 7 and 8 were taken to measure the efficiency of Clairton's physical-chemical and biological treatment systems for cokemaking wastewaters. In August 1977, influent to the coke plant and final effluent after dilution were sampled. The final effluent was mixed with 34.4 percent dilution water; therefore, the LC_{50} of the treated process effluent is estimated as 17.7 percent (0.656×27) which is approximately 290 times less toxic than the untreated water. The influent to the treatment plant was extremely toxic with an LC_{50} of 0.061 percent. Reference 9 presented some qualitative data on Clairton's effluent and stated that toxicity was slight to moderate.

Plant No. 8 includes samples taken during a pilot-scale study of the U.S. Steel, Clairton Works biotreatment system conducted by Environmental Dynamics, Inc. (EDI) in 1980-81 [10]. The system was operated during the tests at conditions selected from bench-scale tests: a hydraulic retention time of 2 days; a volume ratio of dilution water to process water 700/2000; a control target temperature of 30°C (20°-30°C); a dissolved oxygen target level of 4 mg/L (3-5 mg/L); and a pH controlled at 6.8. The results shown are for two separate tests of each system using 100 percent effluent. On the second test, the PAC-containing unit showed toxicity associated with nitrification upsets, presumed to have arisen from oil and grease shock in early October. Effluent ammonia increased substantially at that time. The non-PAC-containing unit, run in parallel, recovered more quickly, and the toxicity test showed 15 percent affected minnows. The LC_{50} for the PAC unit was estimated at 49 percent. The increased toxicity may have been due to abnormally high effluent thiocyanate from the PAC unit. Thiocyanate rose from a norm of 1.0 mg/L to a high of 160 mg/L at the conclusion of the run. Evidently desorption of materials from the PAC inhibited thiocyanate-metabolizing organisms. Other toxic substances that were detected at higher concentrations from the PAC unit were: fluoranthene, 820 µg/L vs. 70 µg/L for the control unit operated in parallel; benzo(a)-pyrene, 20 mg/L vs. nil in the control.

Data from the Pittsburgh Works of J&L Steel also provide an analysis of the treatment system's effectiveness. Wastewaters are subjected to free-ammonia stripping and dephenolization by solvent extraction. The coke-plant wastewater is given a physical-chemical treatment in two different treatment plants. The LC_{50} for the untreated water was 0.46 and 0.65 percent for fathead minnows and waterfleas, respectively. Treatment Plant 1 reduced the toxicity by factors of 10 and 5 for the minnows and waterfleas, respectively. The second treatment plant reduced toxicity by a factor of 6 for both organisms. A comparison of physical-chemical treatment at J&L with the biological treatment at Clairton led the investigators to the following conclusion: the biological treatment at Clairton is much more efficient at reducing toxicity than physical-chemical treatment at J&L. The final effluent at J&L was more toxic, even though the influent at Clairton was much more toxic than J&L's influent [7]. These comparisons must be regarded a applicable at the time tests were made.

The remaining data are for three plants with at least BPT treatment of cokemaking wastewaters. The National Steel data showed no toxicity from a biological oxidation treatment system with two aeration basins operated in parallel, but data for the other two plants suggest a toxicity problem [8,9]. The Shenango plant uses carbon adsorption and alkaline chlorination (the latter to convert cyanides to cyanates), but the resulting effluent was classified "very toxic" [9].

6.2.2 Ironmaking Wastewater Toxicity

The available toxicity data for blast-furnace effluent are summarized in Table 6-4. These data include blowdown from the recycle system alone and in combination with dilution water from noncontact cooling. No tests were conducted on the untreated water; therefore, it is difficult to assess the treatment's effectiveness at reducing toxicity. Chemical analyses are available for many of the samples. Treatment methods were obtained from the referenced reports and supplemented with data reported in Reference 1.

TABLE 6-4. TOXICITY DATA, IRONMAKING WASTEWATER

No.	Plant	Outfall From^a	Treatment^b	Date	Test^c	Organism^d	LC$_{50}$ (%)^e	Reference
1	Ford Motor Co. River Rouge, MI	A^f,C,M	T,VF,(FLP,CT, FP)	10/79	S-48	DM	NM	6
		C,N,O		10/79	S-48	DM	NM	6
		C^g		10/80	S-24	DM	82	12
2	Great Lakes Steel Zug Island, MI	C,O^h	CL,T,VF,(FLP)	12/78	S-48	DM	< 6	4
		C,O		12/78	S-48	DM	NM	4
		C,N		12/78	S-48	DM	NM	4
		C		12/78	S-48	DM	60% Mort.	4
		A^f,C,M,N		12/78	S-48	DM	NM	4
		C,M		6/81	CF-96	PP	<43	5
		A^f,C,M,N		6/81	CF-96	PP	10% Mort.^{i}	5
3	U.S. Steel Pilot Plant South Chicago, IL	C	CL,FLL,CLB, FDSG,CA	8/78	CF-96	LM	NM	13
				8/78	CF-96	NA	NM	13
				8/78	CF-96	PP	5% Mort.	13
4	McLouth Steel Trenton, MI	C,D1,D3 G1,$I1^j$	SL,PSP,SS, FLF,FLL,CL, FLP	9/80	S-24	DM	NM	14

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[a] Processes are coded as prescribed in Reference 1 (Volume 1, pg.338) with additions:

A:	By-product cokemaking
C:	Ironmaking
D1:	Basic oxygen furnace
D3:	Electric arc furnace
G1:	Hot forming
I1:	Acid pickling
M:	Boiler and/or compressor house
N:	Noncontact cooling water
O:	Surface runoff, drainage
P:	Chemical plant and pipe lining

TABLE 6-4. (continued)

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[b] Treatments

ASF: Free-ammonia still
BOA1: Single-stage biological oxidation
BOA2: Two-stage biological oxidation
CA: Carbon adsorption
CL: Clarifier
CLA: Alkaline chlorination
CLB: Breakpoint chlorination
CT: Cooling tower
DP: Dephenolization
FDSG: Filter, deep, sand, gravity
FLF: Flocculation with ferric chloride
FLL: Flocculation with lime
FLP: Flocculation with polymer
FP: Pressure filtration
SL: Settling lagoon
T: Thickener
VF: Vacuum filtration

[c] Type of test:

S-n: Static test for n hours
CF-n: Continuous flow test for n hours

[d] Type of test organism:

CV: Cyprinodon variegatus (sheepshead minnow)
DM: Daphnia magna (waterflea)
DP: Daphnia pulex (waterflea)
LM: Leopomis machrochirus (bluegill sunfish)
MB: Mysidopsis bahia (shrimp)
NA: Notropis atherinoides (emerald shiner)
PP: Pimephales promelas (fathead minnow)

[e] LC_{50} = Effluent concentration lethal to 50 percent of the test organisms:

n% Mortality: Percent mortality in 100-percent effluent reported when LC_{50} cannot be calculated
NM: No mortality

TABLE 6-4. (continued)

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[e] (continued)

NSM: No significant mortality
Mod. Toxic: Moderately toxic
Sl. Toxic: Slightly toxic
V. Toxic: Very toxic

[f] Noncontact water from the coke plant

[g] Blast furnace blowdown

[h] Includes equipment blowdown

[i] Low mortality, but fish were lethargic in concentrations over 25 percent. Suspect volatile organic compounds.

[j] Effluent from a central treatment plant

The first Ford Motor Company sample represents treated blast-furnace water from the thickener overflow after mixing with noncontact water from the coke plant and boiler house. The second sample represents treated blast-furnace water combined with noncontact cooling water from several processes and storm water. No significant toxicity was observed in either sample. The third sample represents only the blowdown from the blast-furnace treatment plant before any dilution. The LC_{50} concentration was reported as 82 percent.

The seven samples from Great Lakes Steel represent several combinations of blast-furnace water with water from miscellaneous sources. The first sample includes treated blast-furnace water, sump drainage, gas-line drips, equipment blowdown, yard runoff, and drainage from the stockhouse and slag pits. This effluent was very toxic with an LC_{50} concentration less than 6 percent. The analyst noted higher than normal pH in this sample (8.6 to 10) and also reported a distinct hydrogen sulfide odor. Chemical analyses were 88 mg/L sulfide and 0.92 mg/L cyanide.

The second Great Lakes sample represents contaminated cooling water from the blast furnaces and yard drainage. The third sample includes miscellaneous process water from the blast furnace after combining with noncontact cooling water and storm runoff. No toxicity was observed in these two samples. The fourth sample includes water from the gas washers, gas coolers, and wet precipitators from all of the blast furnaces after it passes through the clarifiers and thickeners. No mortality was observed at a concentration of 50 percent, and a mortality of 60 percent was observed in the undiluted effluent.

The fifth and seventh Great Lakes samples represent two different toxicity tests on the same outfall at different dates. This outfall includes treated process water from the blast furnace after the clarifier, noncontact water from the coke plant and blast furnace, and boiler-house water. The sixth sample includes only the treated blast-furnace water from the clarifier and some boiler-house blowdown. An LC_{50} of less than 43 percent was observed in a 96-hour continuous flow test of fathead minnows. The analyst believed un-ionized ammonia (NH_3-N) was probably responsible for the toxicity. Un-ionized ammonia estimates ranged from 0.1 mg/L for 6 percent effluent to 3 mg/L for 50-percent effluent. The seventh sample (labeled A,C,M,N) represents the blast furnace effluent after dilution. Although a mortality of only 10 percent was observed in the 100-percent effluent, increasing lethargy was observed in the fish for concentrations greater than 25 percent. The analyst noted that several volatile organic compounds not found in the process water from the blast furnace appeared in the diluted stream and was probably responsible for the developed lethargy [5].

Reference 13 is a study of a pilot-plant process to treat blast-furnace blowdown at U.S. Steel's South Chicago Works. Wastewater from the gas scrubbers is directed to a grit pit for settling of gross dirt, to a clarifier, and then to the hot well of the cooling tower. The water for the pilot system study was removed from the hot well, pH adjusted to 10.7 to precipitate calcium, enriched to contain 5 ppm phenol, and clarified. This process water was subjected to breakpoint chlorination, filtered through a mixed media of anthracite and sand, and then passed through a column of activated carbon. The treated effluent showed no significant mortality to the test organisms.

The contractor also conducted bioconcentration studies of the bluegill sunfish. Chemical analyses of the tissues of the control and exposed fish revealed no significant differences. An egg and fry test was also conducted and yielded a minimum threshold concentration (MTC) of 42 to 65 percent. The MTC is an estimate of the highest effluent concentration tested that did not cause any significant effect on the embryo and fry during the early stages of development [13].

The sample taken at McLouth Steel represents the effluent from the wastewater treatment plant that treats process water from several sources. The treatment plant receives water from the blast-furnace blowdown, basic oxygen furnace, electric arc furnace, hot forming, and acid pickling. The process water is treated initially by some oil and solids removal in scale pits and settling basins at each process. At the wastewater treatment plant, the following processes are used: primary sedimentation, mechanical oil removal, ferric chloride and lime addition, clarification, and anionic polymer addition. No mortality was observed in the treated final effluent.

6.2.3 Steelmaking Effluent Toxicity

The existing data on the toxicity of steelmaking effluent are summarized in Table 6-5. Some of the treated effluent samples represent a combination of process streams. Chemical analyses are available for most of these toxicity samples. Treatment technologies were taken from the referenced reports when

TABLE 6-5. TOXICITY DATA, STEELMAKING WASTEWATER

No.	Plant	Outfall From[a]	Treatment[b]	Date	Test[c]	Organism[d]	LC_{50} (%)[e]	Reference
1	Georgetown Steel Georgetown, SC	D3[f],F,G1	SSP,CT,FDSP, SS	3/78	CF-96	CV	NM	15
					S-96	CV	NM	15
					CF-96	MB	20% Mort.	15
					S-96	MB	NM	15
2	Ford Motor Co. River Rouge, MI	D3[f],N[g]	CL,FLP,SL	10/79	S-48	DM	NM	6
3	Great Lakes Steel Ecorse, MI	D1[f],D3[f]	Untreated	11/79	S-48	DM	NM	16
		D3,I1,J1,M	E,SS,AO,FLF, A,CL	11/79	S-48	DM	10% Mort.	16
				6/80	CF-96	DM	NM	17
				9/81	S-48	DM	NM	18

[a] Processes are coded as prescribed in Reference 1 (Volume 1, p. 338) with additions:

D1: Basic oxygen furnace
D3: Electric arc furnace
F: Continuous casting
G1: Hot forming
I1: Sulfuric acid pickling
J1: Cold forming
M: Boiler and/or compressor house
N: Noncontact cooling water

[b] Treatments

A: Acidification
AO: Air oxidation
CL: Clarifier
CLA: Alkaline chlorination
CT: Cooling tower
E: Equilization of flow
FDSP: Deep-sand filter pressure

TABLE 6-5. (continued)

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[b] Treatments: (continued)

FLF:	Flocculation with ferric chloride
FLP:	Flocculation with polymer
FP:	Pressure filtration
SL:	Settling lagoon
SS:	Surface skimming (oil)
SSP:	Secondary scale pit

[c] Type of test:

S-n:	Static test for n hours
CF-n:	Continuous flow test for n hours

[d] Type of test organism:

CV:	Cyprinodon variegatus (sheepshead minnow)
DM:	Daphnia magna (waterflea)
DP:	Daphnia pulex (waterflea)
LM:	Leopomis machrochirus (bluegill sunfish)
MB:	Mysidopsis bahia (shrimp)
NA:	Notropis atherinoides (emerald shiner)
PP:	Pimephales promelas (fathead minnow)

[e] LC_{50} = Effluent concentration lethal to 50 percent of the test organisms:

n% Mortality:	Percent mortality in 100-percent effluent reported when LC_{50} cannot be calculated
NM:	No mortality
NSM:	No significant mortality
Mod. Toxic:	Moderately toxic
Sl. Toxic:	Slightly toxic
V. Toxic:	Very toxic

[f] Noncontact cooling water from the steelmaking furnace.

[g] Also includes overflow from the slag pits and cooling water from miscellaneous sources.

[h] Approximate breakdown is 25-30% from pickling, 20% from the EAF, and 50-55% from cold rolling.

available and supplemented with data from Reference 1. In general, the treated steelmaking effluent showed little or no toxicity to the test organisms.

The Georgetown Steel plant uses electric arc furnaces to produce steel wire and rod. The wastewater sample is from the steel manufacturing process, cooling water, and runoff before discharge. Potential pollutants include iron, chromium, manganese, grease, and oil. The wastewater from noncontact cooling of the electric arc furnace (dry system), process water from continuous casting, and hot forming are directed to a central treatment plant. Water treatment includes scale pits and settling basins, a cooling tower, deep-sand filters with pressure, and surface skimming for oil removal. The toxicity tests showed a 20-percent mortality for shrimp in the continuous flow test at a 100-percent concentration, but no shrimp mortality was observed for the static test.

The Ford Motor Company sample is also for noncontact cooling from the EAF (dry system), noncontact cooling water from several sources, and overflow from the slag pits. Treatment includes chlorine addition, clarification with polymer addition, and a settling lagoon. No mortality was observed in this sample.

The first sample from Great Lakes Steel is noncontact cooling water from the electric furnace shop and basic oxygen process shop which is discharged untreated. No mortality was observed. The remaining samples from Great Lakes Steel represent the outfall from a central treatment plant which handles wastewater from the electric arc furnace spray chamber, boiler blowdown, filter backwash, pickling rinse water, and cold-rolling wastewater. The breakdown is approximately 20 percent from the EAF, 25-30 percent from pickling, and 50-55 percent from cold rolling. Treatment includes flow equalization, surface skimming, ferrous ion and HCl addition, aeration tanks to oxidize the ferrous ion, acid addition, and clarification. Toxicity tests of this effluent showed no significant mortality.

6.2.4 Hot-Forming Effluent Toxicity

Toxicity data for hot-forming effluent from other sources are summarized in Table 6-6. These data are from two plants, and both cases represent the effluent from the treatment of a combination of process streams. Chemical

TABLE 6-6. TOXICITY DATA, HOT-FORMING WASTEWATER

No.	Plant	Outfall From[a]	Treatment[b]	Date	Test[c]	Organism[d]	LC_{50} (%)[e]	Reference
1	Ford Motor Co. River Rouge, MI	G,I1	PSP,FDO,CL, SS,NC,SL	10/79	S-48	DM	NM	6
2	Great Lakes Steel Ecorse, MI	F,G,M,R	FLP,SB,SS	11/79	S-48	DM	NM	16
		G,N,O,R	SB,SS	11/79	S-48	DM	NM	16
		G,N	SB,SL,SS,FLP	4/80	S-48	DM	10% Mort.	19

[a] Processes are coded as prescribed in Reference 1 (Volume 1, p. 338) with additions:

F: Continuous casting
G1: Hot forming
I1: Sulfuric acid pickling
M: Boiler and/or compressor house
N: Noncontact cooling water
O: Surface runoff, drainage
R: Soaking pit drainage

[b] Treatments

CL: Clarifier
FDO: Deep filter with walnut shells
FLP: Flocculation with polymer
NC: Neutralization with caustic
PSP: Primary scale pit
SB: Settling basin
SL: Settling lagoon
SS: Surface skimming (oil)

[c] Type of test:

S-n: Static test for n hours
CF-n: Continuous flow test for n hours

TABLE 6-6. (continued)

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[d] Type of test organism:

CV: Cyprinodon variegatus (sheepshead minnow)
DM: Daphnia magna (waterflea)
DP: Daphnia pulex (waterflea)
LM: Leopomis machrochirus (bluegill sunfish)
MB: Mysidopsis bahia (shrimp)
NA: Notropis atherinoides (emerald shiner)
PP: Pimephales promelas (fathead minnow)

[e] LC_{50} = Effluent concentration lethal to 50 percent of the test organisms:

n% Mortality: Percent mortality in 100-percent effluent reported when LC_{50} cannot be calculated
NM: No mortality
NSM: No significant mortality
Mod. Toxic: Moderately toxic
Sl. Toxic: Slightly toxic
V. Toxic: Very toxic

analyses of the water sample are available for both of these plants. The descriptions of treatment technology were taken from the referenced reports when available and supplemented with data from Reference 1.

The sample from Ford Motor Company includes treated wastes from the slabbing mill, blooming mill, hot-rolling mill, pickling operations, and a few miscellaneous plant sources. Scale-removal water and contact-cooling water from the wet scrubber on the scarfing operations is discharged to scale pits, filtered, and recycled with blowdown to the treatment plant. Water from the scrubber on the pickling baths and pickle liquor rinse water are neutralized with caustic and sent to the treatment plant. At the treatment plant, the wastewater passes through grit chambers, clarifiers, and oil-polishing lagoons equipped with oil skimmers. The effluent from this treatment plant showed no mortality to waterfleas.

The first Great Lakes Steel sample is treated wastewater from a soaking pit, slab mill, blowdown from the continuous caster and boiler house, and floor drainage from service shops. Polymer is added to the wastewater prior to settling in basins, and floating oils are removed mechanically before the underflow is discharged. No mortality was observed in this effluent.

The second sample listed for Great Lakes Steel includes wastewater from the blooming mill, noncontact cooling water, area drainage from the blooming mill, and drainage from a soaking pit. The wastewater drains to an oil skimmer basin before discharge. No mortality was observed in a 48-hour static test of waterfleas.

The third sample for Great Lakes Steel represents treated process wastewater from contact cooling in the hot-strip mill after the treated water has been diluted with noncontact cooling water. The process wastewater is treated in scale pits, settling basins, settling lagoons with oil skimmers, and flocculated with polymer. Ten-percent mortality of waterfleas in 100-percent effluent was observed for this sample.

6.2.5 Acid Pickling Wastewater Toxicity

The existing data for toxicity of pickling wastewater are summarized in Table 6-7. The data for Ford Motor Company and Great Lakes Steel have been presented previously because they represent a combination of process waste-

TABLE 6-7. TOXICITY DATA, ACID PICKLING WASTEWATER

No.	Plant	Outfall From[a]	Treatment[b]	Date	Test[c]	Organism[d]	LC_{50} (%)[e]	Reference
1	McLouth Steel Gibraltar, MI	I2,J,M	NC,SL	3/78	S-48	DM	NM	20
2	Ford Motor Co. River Rouge, MI	G,I1	PSP,FDO,CL, SS,NC,SL	10/79	S-48	DM	NM	6
3	Great Lakes Steel Ecorse, MI	D3,I1,J1,M	E,SS,AO,FLF, A,CL	11/79	S-48	DM	10% Mort.	16
				6/80	CF-96	DM	NM	17
				9/81	S-48	DM	NM	18

[a] Processes are coded as prescribed in Reference 1 (Volume 1, p. 338) with additions:

D3: Electric arc furnace
G: Hot forming
I1: Sulfuric acid pickling
I2: Hydrochloric acid pickling
J2: Cold forming
M: Boiler and/or compressor house

[b] Treatments

A: Acid addition
AO: Air oxidation
CL: Clarifier
E: Flow equalization
FDO: Deep filter with walnut shells
FLF: Flocculation with ferric chloride
NC: Neutralization with caustic
SL: Settling lagoon
SS: Surface skimming (oil)

[c] Type of test:

S-n: Static test for n hours
CF-n: Continuous flow test for n hours

TABLE 6-7. (continued)

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[d] Type of test organism:

CV: Cyprinodon variegatus (sheepshead minnow)
DM: Daphnia magna (waterflea)
DP: Daphnia pulex (waterflea)
LM: Leopomis machrochirus (bluegill sunfish)
MB: Mysidopsis bahia (shrimp)
NA: Notropis atherinoides (emerald shiner)
PP: Pimephales promelas (fathead minnow)

[e] LC_{50}= Effluent concentration lethal to 50 percent of the test organisms:

n% Mortality: Percent mortality in 100-percent effluent reported when LC_{50} cannot be calculated
NM: No mortality
NSM: No significant mortality
Mod. Toxic: Moderately toxic
Sl. Toxic: Slightly toxic
V. Toxic: Very toxic

waters. The data are listed again in this section because pickling wastewater comprises a significant portion of the treated stream.

The sample from McLouth Steel represents treated water from the pickling rinse, boiler blowdown, acid regeneration scrubber, floor drains, pickling tower scrubber, and pond water from the tandem mill. The treatment consists of neutralization in two stages and settling in lagoons. No mortality to waterfleas was observed in the effluent from this lagoon.

The samples from Ford Motor Company were described in the previous section and include treated wastewater from hot forming, water from the scrubbers on the pickling baths, and pickle liquor rinse water.

The pickling wastewater is neutralized with caustic and delivered to a central treatment of grit chambers, clarifiers, and oil-polishing lagoons with oil skimmers. The treated effluent from the combined processes showed no mortality.

The sample from Great Lakes Steel was previously described in Section 6.2.3, and includes treated water from pickling (25-30 percent), electric arc furnace (20 percent), and cold rolling (50-55 percent). No significant mortality was observed.

6.2.6 Cold-Forming Effluent Toxicity

Some of the data in Table 6-8 have been presented previously because a combination of processes was involved. The sample from McLouth Steel was described in Section 6.2.5. Wastewater from the cold mill is an oil/water solution which is pumped to a pond where acid is added to aid oil/water separation. The pond water is then sent to a central treatment which includes neutralization and settling lagoons. No mortality was observed.

The Ford Motor Company sample includes noncontact cooling water from both the cold-rolling operation and from powerhouse cooling. No treatment is provided, and no mortality to waterfleas was observed. However, daphnids in all test concentrations except the control were observed floating on the surface. The analyst suspected oils in the wastewater (9 to 29 mg/L) caused the test organisms to float.

The sample from Great Lakes Steel was discussed in detail in Section 6.2.3. Approximately 50-55 percent of the process wastewater originates from

TABLE 6-8. TOXICITY DATA, COLD-FORMING WASTEWATERS

No.	Plant	Outfall From[a]	Treatment[b]	Date	Test[c]	Organism[d]	LC_{50} (%)[e]	Reference
1	McLouth Steel Gibraltar, MI	I2,J,M	NC,SL	3/78	S-48	DM	NM	20
2	Ford Motor Co. River Rouge, MI	J[f],M	None	10/80	S-24	DM	NM[g]	12
3	Great Lakes Steel Ecorse, MI	D3,I1,J,M	E,SS,AO,FLF, A,CL	11/79	S-48	DM	10% Mort.	16
				6/80	CF-96	DM	NM	17
				9/81	S-48	DM	NM	18

[a] Processes are coded as prescribed in Reference 1 (Volume 1, p. 338) with additions:

D3: Electric arc furnace
I1: Sulfuric acid pickling
I2: Hydrochloric acid pickling
J: Cold forming
M: Boiler and/or compressor house

[b] Treatments

A: Acid addition
AO: Air oxidation
CL: Clarifier
E: Flow equalization
FLF: Flocculation with ferric chloride
NC: Neutralization with caustic
SL: Settling lagoon
SS: Surface skimmer (oil)

[c] Type of test:

S-n: Static test for n hours
CF-n: Continuous flow test for n hours

TABLE 6-8. (continued)

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[d] Type of test organism:

CV:	Cyprinodon variegatus (sheepshead minnow)
DM:	Daphnia magna (waterflea)
DP:	Daphnia pulex (waterflea)
LM:	Leopomis machrochirus (bluegill sunfish)
MB:	Mysidopsis bahia (shrimp)
NA:	Notropis atherinoides (emerald shiner)
PP:	Pimephales promelas (fathead minnow)

[e] LC_{50} = Effluent concentration lethal to 50 percent of the test organisms:

n% Mortality:	Percent mortality in 100-percent effluent reported when LC_{50} cannot be calculated
NM:	No mortality
NSM:	No significant mortality
Mod. Toxic:	Moderately toxic
Sl. Toxic:	Slightly toxic
V. Toxic:	Very toxic

[f] Noncontact cooling water from cold rolling.

[g] Daphnids floated on surface; suspect oil in the water.

the cold-rolling operation, and the balance is from the electric arc furnace and pickling operations. No significant mortality was observed in the treated effluent.

6.2.7 Hot-Coating Effluent Toxicity

No data were found that evaluated the toxicity of effluent from hot-coating operations.

6.2.8 Combined Effluent Toxicity

Table 6-9 summarizes data on the toxicity of the final combined effluent from three steelmaking facilities. Process streams from all major processes are combined for discharge after various types of treatment. Treatment techniques include some initial treatment at the specific process followed by additional treatment in a central location or dilution with noncontact water after treatment. Samples taken in 1975 at Republic Steel show significant mortality with LC_{50} concentrations of 19.5 and 34.5 percent. The samples taken in 1980-81 at U.S. Steel and McLouth Steel show much lower toxicity in the final treated effluent.

TABLE 6-9. TOXICITY DATA, COMBINED EFFLUENT FROM INTEGRATED PLANT

No.	Plant	Outfall From	Treatment	Date	Test[a]	Organism[b]	LC_{50} (%)[c]	Reference
1	U.S. Steel Fairfield, AL	All Processes	Various	8/81	S-24	PP	NM	2
				8/81	S-24	DP	89.5	2
2	Republic Steel Gadsden, AL	All Processes	Various	5/75	S-48	DM	19.5	21
				5/75	S-96	LM	NM	21
				5/75	CF-96	LM	34.5	21
3	McLouth Steel Trenton, MI	All Processes	Various	9/80	S-24	DM	NM	14

[a] Type of test:

S-n: Static test for n hours
CF-n: Continuous flow test for n hours

[b] Type of test organism:

CV: Cyprinodon variegatus (sheepshead minnow)
DM: Daphnia magna (waterflea)
DP: Daphnia pulex (waterflea)
LM: Leopomis machrochirus (bluegill sunfish)
MB: Mysidopsis bahia (shrimp)
NA: Notropis atherinoides (emerald shiner)
PP: Pimephales promelas (fathead minnow)

[c] LC_{50} = Effluent concentration lethal to 50 percent of the test organisms:

n% Mortality: Percent mortality in 100-percent effluent reported when LC_{50} cannot be calculated
NM: No mortality
NSM: No significant mortality
Mod. Toxic: Moderately toxic
Sl. Toxic: Slightly toxic
V. Toxic: Very toxic

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